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CONTENTS OF VOL. XX, SECOND SERIES

JULY, 1922

Atomic Constants and Dimensional Invariants. A. C. LUNN 1
The Ratio of the Two Elementary Charges. F. W. LOOMIS 15
Radiation from a Group of Electrons. LEIGH PAGE 18
Another Ether-Drift Experiment. ROY J. KENNEDY 26
Note on the Lorentzian Electron. I. MAIZLISH 34
Maxwell's Law of Distribution of Velocities and the Principle of Projective Covariance. I. MAIZLISH 39
A Modification of Van der Waals' Equation. W. P. BOYNTON and ARTHUR BRAMLEY .. 46
The Effect of Nascent Hydrogen on Hard Steel Magnets. JOHN COULSON 51
Improvement in the Determination of the Radium Content of Low-Grade Radium-Barium Salts. VICTOR F. HESS and ELIZABETH E. DAMON 59
The Variation of the Photoelectric Current with Thickness of Metal. OTTO STUHLMAN, JR. 65
Note on the Ratio of Mass to Weight for Bismuth and Aluminum. H. A. WILSON 75
Proceedings of the American Physical Society 78

AUGUST, 1922

On the Nature of the Negative and Positive Ions in Air, Oxygen and Nitrogen. HENRY A. ERIKSON 117
Phenomena in Gases Excited by Radio Frequency Currents. E. O. HULBURT 127
The Effect of the Magnetic Field on the Absorption of X-Rays. JOSEPH A. BECKER 134
The Action of the Bow in Stringed Instruments. K. C. KAR 148
A Study of the Effect of Adsorbed Gas on the High-Frequency Resistance of Copper Wire. AUSTIN BAILEY 154
Electromagnetic Waves in Absorbing Media. LEIGH PAGE 166
A Transition of Adsorption-Layer Theory of the E.M.F. of the Voltaic Cell. R. D. KLEEMAN 174
The Variation of the Residual Ionization in Air with Pressure, for a Range of 57 Atmospheres. K. MELVINA DOWNEY 186
Proceedings of the American Physical Society 194

SEPTEMBER, 1922

The Optical Constants of Sodium-Potassium Alloys. RAYMOND MORGAN 204
Relative Intensities of Stark Effect Components in the Helium Spectrum. JOHN STUART FOSTER 214
Quenching: A Mathematical Study of Various Hypotheses on Rapid Cooling. K. HEINDLHOFER 221
The Stress-Energy Tensor in Electromagnetic Theory and a New Law of Force. H. BATEMAN 243
The Variation of the Index of Refraction of Water, Ethyl Alcohol, and Carbon Bisulphide, with the Temperature. ELMER E. HALL and ARTHUR R. PAYNE 249
Measurement of Mercury-Vapor Pressure by Means of the Knudsen Pressure Gauge. CHARLES F. HILL 259
On the Ageing Effect in the Mobility of Positive Gas Ions. H. B. WAHLIN 267

The Effect of Dissolved Substances on the Deposition of Colloidal Particles from a Solution by Means of an Electric Current. RICHARD D. KLEEMAN 272
The Hall-Ettingshausen, Nernst and Leduc Effects in Cadmium, Nickel and Zinc. A. E. CASWELL 280

OCTOBER, 1922

Theory of Ionization by Cumulative Action and the Low-Voltage Arc. KARL T. COMPTON 283
The Thermionic Work Function of Tungsten. C. DAVISSON and L. H. GERMER 300
The Relative Sensitivity of the Ear at Different Levels of Loudness. DONALD MACKENZIE 331
The Optical Properties of Molten Metals. A. K. ASTER 349
Bombardment of Metal Surfaces by Slow-Moving Electrons. H. E. FARNSWORTH 358
Note on the Specific Heat of Tungsten. PAUL F. GAEHR 375

NOVEMBER, 1922

The Mobilities of Electrons in Hydrogen. LEONARD B. LOEB 397
The Scattering of X-Rays by Crystals. G. E. M. JAUNCEY 405
The Effect of Temperature on the Scattering of X-Rays by Crystals. G. E. M. JAUNCEY. 421
The Crystal Structure of Silver-Palladium and Silver-Gold Alloys. L. W. MCKEEHAN. 424
Detecting Efficiency of the Resistance-Capacity Coupled Amplifier to 6,000 Meters. W. G. BROMBACHER 433
The Thermoelectromotive Force of Copper-Manganese Alloys. SKEZUG KIMURA and ZUNEHACHI ISAWA 441
Note on Overblown Pipes. S. SHARGAVA and R. N. GHOSH 452
The Energy Losses Accompanying Ionization and Resonance in Mercury Vapor. JOHN A. ELDRIDGE 456
Electrical Conduction Across Minute Air-Gaps. JAMES W. BROXON 476
The Effect of Certain Dissolved Substances of the Infra-red Absorption of Water. J. R. COLLINS 486
The Existence of High-Mobility Ions. OSWALD BLACKWOOD 499

DECEMBER, 1922

A Photographic Study of Sound Pulses between Curved Walls and Sound Amplification by Horns. ARTHUR L. FOLEY 505
An Experimental Investigation of the Dispersion of a Limited Wave Train. IRVIN S. HOLT 513
Note on Musical Drums. R. N. GHOSH 526
Acoustic Wave Filters. G. W. STEWART 528
A Study of the Exciting Power for Fluorescence of the Different Parts of the Ultraviolet Spectrum. LELAND JAYNES BOARDMAN 552
Spectra of Hydrogen, Nitrogen and Oxygen in the Extreme Ultraviolet. J. J. HOPFIELD. 573
The Variation of Metallic Conductivity with Electrostatic Charge. F. WENNER, NYNA L. FORMAN and A. R. LINDBERG 589
Reciprocal Diffraction Relations between Circular and Elliptical Plates. JOHN COULSON and G. G. BECKNELL 594
Heat Flow in a Finite Cylinder having Variable Surface Temperature. GEORGE E. THOMPSON 601
An Extension of the Principle of the Diffraction Evolute and Some of its Structural Detail. G. G. BECKNELL and JOHN COULSON 607
New Evidence Regarding the Interpretation of Critical Potentials in Hydrogen. P. S. OLMSTEAD 613
Positive-Ray Analysis of Potassium, Calcium and Zinc. A. J. DEMPSTER 631

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Properties of Rochelle Salt related to the Piezo-electric Effect. JOSEPH VALASEK..... 639
Low-Voltage Arcs in Diatomic Gases. O. S. DUFFENDACK........................ 665
An Experimental Study of the Scattering of Approximately Homogeneous X-Rays by Powdered Crystalline Carbon, Metallic Lithium, and Liquid Benzene Mesitylene and Octave. C. W. HEWLETT.. 688
Absorption Coefficients for Homogeneous X-Rays. E. G. TAYLOR.................. 709
A Second Undamped Wave Method of Determining Dielectric Constants. A. P. CARMAN and G. T. LORANCE.. 715
On a New Method for the Generation of Sound Waves. JUL. HARTMANN........... 719
On the Influence of the Surface-Tension on the Efflux of a Liquid in Jet Form. JUL. HARTMANN.. 728
Erratum.. 745
Index.. 747

Second Series *July, 1922* *Vol. XX., No. 1*

THE

PHYSICAL REVIEW.

ATOMIC CONSTANTS AND DIMENSIONAL INVARIANTS

By A. C. Lunn.

Synopsis.

Dimensionally Invariant Products of Universal Physical Constants.—The number of experimentally determined universal constants is well known to be greater than the number of the fundamental independent units of measurement. The excess quantities should be expressible in terms of the others, that is, there must exist a number of dimensional invariants equal to this excess. Invariants which have a theoretical basis serve to check experimental values, and others also may be useful in suggesting numerical relations not otherwise suspected. As an illustration, this paper lists seven quantities which are dimensioned in length, time and mass only: e, the ratio of the electronic charge to the root of the dielectric constant; m, the electronic mass; $b = k^4/4^6\pi^6 a$, where k is the Boltzmann constant and a the coefficient of black radiation density; $f = h/2\pi$; n, the Rydberg wave-number; c, the velocity of light; and γ, the gravitation constant. In terms of these there must be four independent invariants, for instance: $c^3f^3/b = P$; $e^2/cf = S$; $\gamma m^2/e^2 = G$; $ne^2/mc^2 = E$. There are also many other relations, such as: $b/e^6 = L = 1/PS^3$; $\gamma^3 m^6/b = G^3/L$; $mc/fn = S/E$; and $\gamma mn/c^2 = GE$. The only theoretical relations now known are: $P = 2^{12}\pi^8/15$, from the Planck spectrum distribution theory, and $4\pi E = S^3$, from the Bohr spectrum theory; both agree with experiment within 0.2 per cent. If in accordance with the Lewis-Adams suggestion we put L equal to 1 instead of 0.995, then Millikan's value of e must be too high by 0.5 per cent. Since S has the value 0.00730, $1 + S + m = 1.0078$, the atomic weight of H, and $4 + 2m = 4.0011$, the atomic weight of He; therefore S may equal the "packing effect." Various numerical formulæ for S are given, such as $3^2/5^3\pi^2$. If M_1 and M_2 are the ratios of the atomic masses of H and He, respectively, to that of an electron, $S^2M_1 = \pi/2^5$, and $S^2M_2 = 5^2/2^6$, within 0.1 per cent. Other similar numerical coincidences which may or may not have theoretical significance are given, for instance: $S/EM_1 = 2^7$; $E^6/GS = 1/2$; $G = 3(E/M_1)^4(1 - 2S)$.

IT has been recognized for some time that the number of universal quantities revealed by physical measurements, but not yet utilized for the practical reduction of the system of arbitrary units, is more than sufficient to complete that reduction so as to give for every sort of measurement a kind of natural unit. Since in most cases the measurements are not yet accurate enough for putting this reduction into effect, it is convenient to retain consideration of these quantities as having dimensions corresponding to the scheme of units as it stands before the reduction is made. The redundancy means that the excess quantities should be expressible in terms of the others, and several relations of this kind have been proposed. Equivalently, there must exist a set of independent dimensionless expressions, or "dimensional invariants," expressible entirely in terms of the quantities of the list and equal in number to the excess.

Because of the differences in precision of different types of measurements it has been customary to adopt as basis a set of the better determined values, equal in number to the arbitrary or primitive units in the dimensional scheme, and for comparison with observed data to express the others in terms of these so far as suitable algebraic relations are at hand from theoretical sources.[1] There is some advantage, however, in avoiding restriction to such a preferential solution through the direct computation of a fundamental set of invariants. The influence of errors of observation in all the quantities concerned can be shown by simultaneous consideration of all the corresponding differential corrections, and a kind of test of the completeness of a theory is found in the number of independent invariants whose theoretical and observed values are in practical agreement. The intent of this paper is to examine the present state of theory from such a point of view, and to compare data from various experimental sources in connection with invariants which have had theoretical values deduced. There are also proposed, for enough further invariants to complete a fundamental list, certain tentative values so accurate as to suggest the possibility of deduction from a theory, and such as to give in particular, simple formulas for the action constant and constant of gravitation. Measured quantities are denoted by small letters and invariants by capitals.

The quantities to be included are the charge e and mass m of the electron, the bielectric coefficient of a vacuum ϵ; the Boltzmann constant k and the coefficient a of black radiation density; the Planck constant h, Rydberg wave-number n, velocity of light in vacuum c, and constant of gravitation γ. There are nine of these, to be considered as dimensioned in five primitive units, say the familiar three of mechanics, together with temperature and one electrical unit. Since the temperature unit affects only k and a, and the electrical unit only e and ϵ, it will be sufficient to consider only the ratios k^4/a and $e/\epsilon^{\frac{1}{2}}$, which are dimensioned in L-T-M only. The latter ratio may as well be denoted by e simply, and it proves convenient to use $k^4/a(4\pi)^4 = b$ say, also in place of h to use $h/2\pi = f$ say, the natural unit of angular momentum. There are then the seven quantities e, m, b, f, n, c, γ, dimensioned in L-T-M simply, and therefore having a fundamental system of four invariants.

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[1] Compare for example the computations in Sommerfeld: Atombau und Spektrallinien, ed. 2, pp. 367–370; Flamm, Phys. Zeitsch., 18, 515–521, 1917; Allen, Proc. Phys. Soc. London, 27, 425–431, 1915; Millikan, PHYS. REV. (2), II., 109–143, and Phil. Mag. (6), XXXIV., 1–30, 1917; Birge, PHYS. REV., (2), XIV., 361–368, 1919.

Together with these four there needs to be considered any relevant ratio of two quantities of the same kind which are not interpreted in terms of each other by a counting process. So far as is known all charges are integral multiples of e, and the b, γ, c, and h are unique, though there seems to be some possibility that the slopes of the photo-electric lines for different elements may prove to involve slightly different individual factors, as well as a universal h, when a precision is reached comparable with that of the various wave-numbers of metallic series. So far as is satisfactorily made out the latter are expressible in terms of the universal n and certain functions of integers together with factors depending on mass-ratios. Moreover, there seems to be increasing probability that all pure atomic species will prove to have atomic weights integrally related to hydrogen or helium or some compromise of these, and the suggestion doubtless remains acceptable, though not yet definitely successful, that the departure of the helium-hydrogen ratio from the integral value may be explainable by an overlapping of fields or "packing effect," or something similar. This would leave the single mass-ratio of hydrogen atom to electron to be explained, but since there are no isotopes of either hydrogen or helium known it seems best to consider both of these mass-ratios, $m_1/m = M_1$ for hydrogen and $m_2/m = M_2$ for helium, as requiring interpretation. A theory of matter can hardly be considered satisfactory until it reaches some interpretation of these ratios, rather than treating them as primary data, but for the present purpose it is suitable simply to annex them to the list of invariants to be studied.

The list of quantities might be taken to include also the gas constant and Faraday constant per mole, but since this involves the use of an additional unit, the chemical mole, there would be only one more invariant, which can be taken as kcF/Re of value unity. Further, the specific charge η can be treated either as abbreviation for e/cm or as a distinct quantity associated then with the invariant $cm\eta/e$, also unity. The number of outstanding invariants required is the same as before.

The algebraic work of determining invariants as products of powers need not be detailed. Since it is likely that the more direct results of theory will be concerned with relatively simple invariants there is convenience in arranging according to number of factors. Examination shows that in the list of seven quantities named there is only one pair, (b, e), which yields a two-letter invariant, only four triples, (c, f, b), $(e. c, f)$, (γ, m, e), (b, γ, m), giving three-letter invariants, and that between these five there are two relations, so that to complete a fundamental system an invariant in four or more letters is needed, to be taken here as formed from (e, c, m, n). The following notation will be used and the identities are indicated.

$$\begin{gathered} b/e^6 = L,\ c^3f^3/b = P,\ e^2/cf = S,\ \gamma m^2/e^2 = G, \\ ne^2/mc^2 = E;\ \gamma^3m^6/b = G^3/L,\ PLS^3 = 1. \end{gathered} \tag{1}$$

The L occurs in the paper of Lewis and Adams,[1] the S is identical with Sommerfeld's α and Allen's q (loc. cit.), the G is a ratio of gravitational and electrostatic forces, and the E can be read as ratio of two energies, the electrostatic potential energy of two elementary charges at a distance of one Rydberg wave-length and the energy corresponding in Einstein's sense to the mass of the electron. In general these four will be taken as fundamental, but a separate notation is taken for the P because of its occurrence in connection with Planck's radiation formula. The writer has also computed all further four-letter invariants and determined their values in terms of the four named. As examples may be noted $mc/fn = S/E$, which may be interpreted as ratio of two angular momenta, and $\gamma mn/c^2 = GE$, a ratio of energies per unit mass. Some of these other invariants may prove of interest in connection with future theories, but the present state of the problem can be described in terms of those already given. The values of all four would need to be known in order to give specific form and full effect to the vague but suggestive theory of Lewis and Adams concerning the ultimate rational units.

There are required then six independent relations for the determination of the four fundamental invariants and the two mass-ratios. Two such relations have been deduced from theories, one coming by integration from the Planck spectrum distribution formula, the other being Bohr's formula for the Rydberg constant. These relations in the present notation are

$$P = 2^{12}\pi^8/15, \tag{2}$$

$$4\pi E = S^3, \tag{3}$$

and their accordance with experimental data is known to be as accurate as the measurements used. Other equations already proposed and those to be added in this paper are to be understood simply as possibly deducible from some theory and by their form possibly suggestive of some features of such a theory, although in any case a relation between invariants represents an experimental fact with whatever precision it proves to have, even if its theoretical connections are unknown. Of the latter type is the relation suggested by Lewis and Adams, namely

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[1] PHYS. REV., (2), III., 92–102, 1914.

$$L = 1 \tag{4}$$

which is so close and simple as to have high probability.

The relations suggested by Allen are not included here, since they are not relations between invariants and depend for their particular form on the use of special units and the decimal scale of notation. A relation proposed by Haas,[1] equivalent in the present notation to $\log G = -2M_1^{\frac{1}{2}} \log \pi$, involves only invariants, but its plausibility is difficult to estimate, partly because a small percentage change in M_1 corresponds to a much larger percentage change in G, about fifty times as large, so that data now known are rather rough to test it. If really correct, however, it yields an accurate value of M_1 for that reason.

Initial test computations will be made with the following data: $n = 109737$, $c = 2.999 \times 10^{10}$, $\gamma = 6.675 \times 10^{-8}$, $e = 4.774 \times 10^{-10}$ $h = 6.545 \times 10^{-27}$, $F = 9649.4$, $\eta = 1.767 \times 10^{7}$, $ca/4 = 5.72 \times 10^{-5}$, giving $m = 9.009 \times 10^{-28}$, $a = 7.629 \times 10^{-15}$, $b = 1.178 \times 10^{-56}$, $f = 1.042 \times 10^{-27}$; and with $M_1 = 1845$, $M_2 = 7328$, corresponding to atomic weights 1.0077 and 4.0020, though the precise values and meaning of these ratios is one subject of discussion.

From these data come $P = 2.588 \times 10^{6}$, $S = 7.295 \times 10^{-3}$, $E = 3.087 \times 10^{-8}$, $G = 2.377 \times 10^{-43}$. Sommerfeld's value of S, computed directly from spectrum data, is 7.290×10^{-3}, but since this comes from the observed separation of components of fine structure having each some outstanding broadening and asymmetry the measurements are not accurate enough to distinguish this value from the other or from the hypothetical values to be mentioned. The values of $15\,P/2^{12}\pi^{8}$, $4\pi E/S^{3}$, and L, which would all be unity according to the equations cited, are respectively .9985, 9989, .9952. Evidently any one of these relations separately can be regarded as exact without stretching the range of uncertainty in the data, but the question is rather whether a single system of differential corrections of admissible magnitude could be applied to the data so as to satisfy all three relations at once. A least square solution with a tentative set of weights gave corrections to both e and η rather dubiously large, but since the assignment of weights to such varied data is precarious the dilemma involved is better shown as follows.

The Planck and Lewis-Adams equations, because of the identity connecting P, L, and S, determine a hypothetical value of S by

$$S_{PL}^{3} = 15/2^{12}\pi^{8},\ S_{PL} = 7.281 \times 10^{-3}, \tag{5}$$

which by itself is clearly admissible; but the inclusion of the Bohr equation gives for E a value

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[1] Haas, Phys. Zeitschr., 19, 330, 1918.

$$E_{PLB} = 15/2^{14}\pi^9 = 3.071 \times 10^{-8}, \tag{6}$$

whence $E/E_{PLB} = 1.005$. There seems to be no known reason for regarding the Rydberg constant as other than sensibly exact for the present purpose or the velocity of light as more uncertain than to the extent of a unit or so in the fourth figure, so that the implication of this last ratio is practically that the product of the measured values of e and η is ½ per cent. too high. Since the η has been measured in a variety of ways by a number of observers and checked by Sommerfeld's spectrum computation with such consistency as not to encourage a reduction of more than one part in 500 or so, the value assumed being probably already low, it appears that the validity of all three relations mentioned is likely to mean that Millikan's value of e is too high by nearly four or five parts per thousand, and that h requires an accompanying correction to keep reasonable accord with the photo-electric and x-ray data.

An uncertainty of that magnitude in measurements by the oil-drop method is doubtless conceivable and need not be ascribed solely or chiefly to instrumental errors unrecognized. There remains unexplained the unexpected lack of difference between solid particles and liquid drops of different viscosities,[1] which may point to some uncertainty as to what is the effective hydrodynamical radius in the application of Stokes' formula; or the hydrodynamical theory may be at fault in other ways, for instance because of the minute scale of the motions or because of the effect of compressibility of the medium, although no such corrections are known to be needed except the allowance for surface slip which was consistently made.

At present, however, the data make it somewhat doubtful that all three relations can be exactly valid, unless possibly by way of some slight change in meaning of some of the symbols. Because of its lack of a specific theoretical background that of Lewis and Adams seems most likely to be only a close approximation. The Planck theory is however fairly obscure in places and further refinements might change the spectrum formula slightly so as to alter the value of P without loss of accord with measurements on total radiation and spectrum distribution. The Bohr formula seems less likely to need amendment, not so much because its theory is altogether satisfactory as because of its wide range of contact with spectrum data, but in view of the influence of motion of the nucleus and the relativity corrections it seems not impossible that other factors may affect the determination of the ideal or asymptotic Rydberg constant to which the formula refers.

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[1] Silvey, PHYS. REV. (2), VII., 87 and 106, 1916.

There seems to be no such difficulty in accepting any two of these relations without the third. The dilemma described can be relieved merely by supposing that (3) is not quite exact; conceivable substitutes for $L = 1$ nearer the computed value will occur in the following; while equations (3) and (4) without (2) leaves S undetermined and its elimination gives simply $4\pi EP = 1$, the computed value being 1.0038, not seriously different in view of the number of factors involved. To illustrate these possibilities it may be mentioned that Millikan's e and Duane's latest value for h,[1] 6.556×10^{-27} using the same e, tend to favor the Lewis-Adams relation rather than the Bohr, giving $S = 7.283 \times 10^{-3}$, curiously near to S_{PL}. Though the estimates of uncertainty given by these observers are somewhat more than enough to cover the discrepancy the numbers as they stand would require in order to satisfy (3) a ½ per cent. reduction in η. But the Einstein quantum relation used in reducing the x-ray data may itself be in need of refinement by factors approximately unity but specific for particular substances; this would be only natural perhaps in view of the nucleus and relativity corrections that improved on Bohr's original equation. Moreover, a complete review of these problems might even find some uncertainty concerned with the Faraday constant, defined in connection with a heavy atom and used for such important purposes in connection with the lightest ones; and this not only because of the recognized difficulties in the way of verifying the Faraday law with the required precision over the whole range of atomic weights. The theory of electromagnetic mass has made familiar the notion of "mutual" mass, whose main descriptive content is concerned with the idea that the summational property of mass may cease to be valid for sufficiently fine subdivisions of matter. This suggests that the strict proportionality of weight, mass, and number of ions may be true only for aggregations of sufficient size to blur out differential effects due to characteristic differences between positive and negative electrical constituents. In such a case the ratio of inertias of individual ions might not agree with the ratio of the large scale chemical equivalents. Positive-ray analysis may reach precision enough to give this possibility a definitive test. At present the prospect is that any such correction would be unimportant for complete atoms.

Related to this is the reason for including the gravitation constant in the present list, namely the widely cherished conviction that gravitation should be interpretable as a residual electromagnetic effect. Some attempts at such a theory seem rather bizarre, and those involving arbitrary statistical assumptions are not likely to be satisfying, one aspect of the difficulty being the very smallness of the residual required, as reflected in the minuteness of the invariant G; but now that fundamental differences between positive and negative electrification are experimentally real the outlook seems more hopeful. Since the idea is used here only as a hint, indication may be deferred as to how it can be considered to harmonize with Einstein's interpretation of the gravitational field.

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[1] Proc. Nat. Acad. Sc., 7, 237–242, 1921.

There are many examples of successful formulas whose construction to fit empirical data antedated their deduction from theory; the Planck and Balmer-Rydberg formulas are examples. It may be not altogether idle, therefore, to search for further numerical coincidences and test them out in various combinations. Especially may be noted such relations as may be in general form suggested by tentative considerations of theory, but too vague to determine for instance certain numerical coefficients.

Aside from the gravitational formula, the kernel of the problem seems likely to be the determination of the invariant S, which is already fundamental in Sommerfeld's theory and will doubtless prove to be of much wider importance. A theoretical explanation of its meaning and value will probably mark the achievement of a satisfactory logical connection between the electron theory and the quantum theories. One suggestion concerned with this outlook appears with the following items, which may not be accidental; fuller developments and alternative interpretations are saved for a special paper.

First, the expression $1 + S$ has value 1.00729, uncertain hardly as much as two units of the last place; addition of .00055, the "atomic weight of an electron," gives 1.00784, agreeing with the atomic weight of hydrogen as closely as that can be considered known. Addition of two electrons, .00109, to even 4.00000, gives conceivable atomic weight of helium differing from Heuse's value 4.002 less than his estimate of uncertainty .0017. The suggestion thus emerges that S may give a kind of measure, to first approximation perhaps, of the "packing effect" or influence of mutual terms which determines the departure of the helium-hydrogen ratio from the even integer.

Second, the notion of "mutual" mass suggests trial of a quadratic function of the atomic number, so as to represent atomic weight as the sum of a term proportional to the number of constituent particles and a term proportional to the number of pairs of particles. The formula $w = 2N + SN^2$ does in fact give quite well the general trend of atomic weights, especially when reduced to the definitional scale $w = 16$ for $N = 8$.

Because of the identity any trial value of S determines a corresponding value of the product PL, and hence with Planck's value of P leads to a substitute for (4); but the partitioning between these two factors is better treated as a separate problem, these two invariants being the only ones used that contain the radiation constant a while their product is not affected by it.

If equation (3) is valid the range of uncertainty as to the value of S is rather narrow, in fact sifting of the data with that equation assumed shows only a small chance that it lies outside the limits .007270 and .007310; if only the values of e, h, and c directly concerned in the definition of S be considered the range is not seriously larger, since the value of h in terms of e by the x-ray method has given such closely consistent results. It was noticed by Jeans[1] that the value of $16\pi^2 S$ is approximately unity, but this is only a rough guess, the computed value being 1.152. On the other hand the value proposed by Page[1] amounts to $S = 3/128\pi = .00746$, which is pretty high to be plausible.

One can hardly have much hope of obtaining a true theoretical value of such a constant by pure conjecture based on numerical coincidence merely, as is illustrated by the following list of numbers, any one a conceivable value of S: $32/45\pi^4 = .007300$, $7/960 = .007292$, $\pi/2^4 3^3 = .007272$, $11/480\pi = .007294$, $7/\pi^6 = .007281$, the fourth being practically the computed value and the last indistinguishable from S_{PL}. The possibility $S^3 = 3^3 2^{11}/5^6\pi^{14}$, $S = .007293$, is curious on account of the corresponding value $E = (24/25\pi^5)^3$. Some of these lead to sets of formulas on the whole fully as simple and plausible as those using the Lewis-Adams relation. But since such trials could be extended indefinitely, and since the coefficients in the later formulas to be proposed are similarly tentative it will be sufficient illustration of the possibilities to consider a single alternative. Since reasons have been given for supposing that the S_{PL} is likely to be too low, it is desirable to have an alternative toward the upper part of the admissible range. Accordingly is suggested for particular trial the new hypothetical value

$$S_H = 3^2/5^3\pi^2 = .007295, \qquad (5a)$$

being practically the computed value, and with (3) giving

$$E_{HB} = 3^6/2^2 5^3\pi^3 = 3.089 \times 10^{-8}, \qquad (6a)$$

also practically as good a fit as the data require. Combination with (2) gives for (4) the substitute value $L = 5^{10}/2^{12}3^5\pi^2 = .9941$. But the possibility must be faced that the true value of S is no such simple thing at all. For example, if it measures some kind of coefficient of stability in atomic structures concerned with the mutual influence of overlapping fields its physical meaning might be quite perspicuous but its numerical value determined only by some trancendental process. Similar remarks of course apply to guesses for other invariants, though such trials may lead to suggestions of promise. For instance, $(10 + \sqrt{5})^3 = 1832.0$, which may point to some trigonometric meaning for the apparent reciprocal atomic weight of the electron.

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[1] Proc. Nat. Acad. Sc., 6, 115–122, 1921.

Since the known quantum phenomena are concerned not so much with the electron alone as with its relation to the various material atoms or nuclei, there is a prospect that the S may have something to do with the differences between positive and negative electricity. The chief known feature of these differences lies in the relatively small inertia of the universal negative electron as compared with the various positive nuclei. Hence there is likely to be some direct connection between S and a mass-ratio, though some uncertainty must be recognized as to what mass-ratio is most directly concerned. The distinction between the mass of an atom and that of its nucleus is at present rather trivial on account of errors in other data, but because of the $\frac{3}{4}$ per cent. departure of hydrogen from the integral value on the oxygen scale and the outstanding uncertainty as to the atomic weight of helium there remains the question as to what is the most directly natural theoretical unit of atomic weight. The notion of the proton as a universal constituent of all atoms suggests the hydrogen scale, the universality of the alpha particle in radioactivity suggests the helium scale, while the fact that the basic processes of measurement employ apparatus constructed largely of solid matter in bulk consisting of heavier atoms invites consideration of other possibilities. In connection with the following formulas it may be decided in particular cases whether M_1 and M_2 are to refer to the neutral atoms or to the nuclei, but the precision reached demands systematic distinction between the actual hydrogen-electron ratio M_1 and the reciprocal atomic weight of the electron, M say, on any chosen scale of atomic weights.

The order of magnitude of S, M_1, and M_2 suggests first consideration of the products SM_1 and SM_2, whose computed values are 13.46 and 53.46, the latter being close to $160/3 = 53.33$; but a form of relation more likely to be directly theoretical seems to be approached in the following way.

The electromagnetic radius of an electron on the hypothesis of a uniform volume distribution of charge is $4e^2/5c^2m = r$ say; the corresponding radii for hydrogen and helium nuclei are $r_1 = r/M$, and $r_2 = 4r/M_2$, these two being only slightly different because of the double charge of helium. An inquiry as to the meaning of these hypothetical "radii" in the light of the theory of relativity led to examination of the geometric means $r_{01} = (rr_1)^{\frac{1}{2}}$ and $r_{02} = (rr_2)^{\frac{1}{2}}$, and it was noticed that the unit of angular momentum f was nearly the same as $4m_1cr_{01}$, the computed coefficients of 10^{-10} being 1.042 and 1.045. The factor 4 suggests examination of m_2cr_{02} which gives coefficient 1.041. Expressed in terms of the invariants these alternative trial relations become

$$SM_1 = 5/16 \quad , \quad SM_2^{\frac{1}{2}} = 5/8 \qquad (7a,\ 7b)$$

the computed ratios of left to right members being 1.0029 and .9993. Although the helium ratio gives here the better fit it is worth noting that if the hypothetical value S_{PL} be used the hydrogen relation becomes practically exact. The true relation may be some compromise deducible from some theory capable at the same time of explaining the departure of M_2/M_1 from the even 4. Though less simply interpretable an alternative possibility for the numerical coefficient appears from the fact that the computed value of S/EM_1 is 128.08, suggesting the first of the following, the second resulting from combination with (3),

$$S/EM_1 = 2^7 \quad , \quad SM_1^{\frac{1}{2}} = (\pi/32)^{\frac{1}{2}},\ SM_2^{\frac{1}{2}} = (\pi/{}^{8})^{\frac{1}{2}}, \qquad (8,\ 7c,\ 7d)$$

The left to right ratios of the last two are 1.0002 and .9966, the hydrogen formula here giving practically perfect fit. Since $8\pi/25 = 1.0053$ there is a curious possibility that both (7*b*) and (7*c*) might be valid if the atomic weight of helium were about 4.008; or (7*c*) and (7*a*) might correspond respectively to the true hydrogen and to some ideal unit of atomic weight. To decide between such closely agreeing alternatives requires greater certainty as to the values of the factors than is now to be had, the difference between (7*a*) and (7*c*) for instance being about $\frac{1}{3}$ per cent. Elimination of between (3) and (7*c*) gives

$$E^2M_1^3 = \pi/2^{19}, \qquad (9)$$

which shows test-ratio .9991 and does not involve the Planck constant. It is of course to be understood that any equation encountered as a result of combining other equations may prove to be valid independently of the validity of the particular relations through which it is initially arrived at. There may also be possibly useful suggestions obtained by writing the same equation in different forms. For instance equation (8) is equivalent to $fM_1 = cm\lambda/128$, where λ is the Rydberg wave-length $1/n$ and the left member is what the angular momentum of a proton would be if it revolved with the same speed and in the same size orbit as would give an electron the unit of angular momentum. There may be a hint here of some connection with the idea which associates the number

128 with a hypothetical decomposition of the hydrogen nucleus, 1/128 being .0078.[1]

A first suggestion for a gravitation formula is found in

$$2E^6/GS = 1, \tag{10}$$

the computed left member being .9975. Insertion of E from (3) gives

$$G = S^{17}/2^{11}\pi^6, \tag{11}$$

with left to right test-ratio .9963. This is a close fit in view of the high exponent of S, which also suggests however that a theoretical deduction would be likely to be rather indirect. Equation (3) and suitable relations of type (7) would make it possible to express in terms of S alone any function of E, S, and mass-ratios; and further forms would result by partial substitution of an assumed value for S.

There is also a certain artificiality in the use of G, which is expressed entirely in terms of electron constants. Since gravitation between electrons is purely hypothetical there is better chance of direct physical meaning, for instance in $G_1 = GM_1^2 = \gamma m_1^2/e^2$ or its helium mate, which with aid of an equation of type (7) would be according to (11) a multiple of S^{12}. It is also likely in this connection to be more fitting to use instead of the pure electron invariant E, similarly modified expressions like $E_1 = E/M_1 = ne\eta_1/c$ where $\eta_1 = e/cm_1$, or $E_{01} = E/M_1^{\frac{1}{2}} = ne^2/c^2(mm_1)^{\frac{1}{2}}$, which treats proton and electron symmetrically.

Another hint is to seek a formula not containing the action constant, say by elimination of S through some combination of (3) and a (7), so as to give G in terms of E and some M's.

A formula of this type, found in fact before (10), is

$$G = 3(E/M_1)^4 \equiv 3E_1^4 \tag{12a}$$

with test-ratio 1.012; this may be written $G_1 = 3E_{01}^4$. If the ideal M be used instead of M_1 the ratio is .9815. These errors are nearly enough equal and opposite to suggest the geometric mean, giving

$$G_1 = 3E^4/M^2, \tag{12b}$$

which tests .9967, which is at least as close as the data are known. The form of these equations seems prepossessing from the point of view of gravitation as a residual electrical effect. It is hardly surprising that the problem of the packing effects and the natural unit of atomic weight should be concerned here also, or that there should be initial uncertainty as to what mass-ratio can be taken as representative of the common properties of matter in bulk. In view of the earlier suggestion of the possible bearing of the invariant S on that problem it is conceivable that the right members here need refinement by factors, for instance in the form of power series in S, with initial term unity, after the manner of Sommerfeld's improved formulas for series of the Balmer type. In fact (12*b*) is practically equivalent to a modification of (12*a*) of the form $G = 3(E/M_1)^4 (1 - 2S\cdots)$. Since $E/M_1 = 5r_1/4\lambda$ in the notation already used it is seen that these equations exhibit ratios of gravitational to electrical forces as proportional to the fourth powers of ratios of electrical to optical lengths. The possible meaning of any one equation naturally appears in somewhat different lights according to what quantities are used in writing it and which are thought of as fundamental. Other possibly significant combinations of equations of the types already given are readily obtained.

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[1] Hinrich, Rev. Gén. d. Chim. pure et appl., 13, 351–354, 1910.

These various trial equations are proposed primarily as individual possibilities, but the basic problem is to obtain a complete set of equations, giving the full number of possible independent relations between the invariants simultaneously in harmony with experimental data. Since such a set has not hitherto been reached by theory or by conjecture it seems worth while to exhibit the following two samples as close approximations, the first being an extension of the original triple (2, 3, 4), the second using in effect a substitute for (4) while retaining the others.

In each case the program is to choose for trial a set of six independent hypothetical relations and by a least square adjustment find differential corrections to the initially assumed values of the seven dimensioned quantities and the two mass-ratios so that these relations are all satisfied. In general a suitable choice of weights for such a purpose would be more or less conjectural as well as the equations, and would influence the result importantly. In the present instance, however, the quantities m, c, F, equal in number as it happens to the number of primitive units, are by common judgment understood to be known with much greater precision than the others. Any reasonable set of weights then leads to a solution such as to leave the values of those quantities practically untouched, and in effect, to the number of decimal places sought, to determine the others in terms of them. The two illustrations may as well then be set forth in the latter sense.

Hypothesis I.—Equations (2, 3, 4) are all taken as valid, so S is determined by (5) then E by (3). The mass-ratio 1842.2 found from (7*a*) is assumed to be for the nucleus, giving 1843.2 for the H-atom, whose atomic weight is supposed to be $1 + S + .00055 = 1.00783$, hence $M = 1829.9$, and $\eta = FM = 1.7648 \times 10^7$. The value of E then yields $e = 4.756$

$\times 10^{-10}$, and that of S determines $h = 6.509 \times 10^{-27}$. The low value of the product $e\eta$ was earlier shown to be unavoidable under these assumptions and the partition seems reasonable. The value of $h/e^{4/3}$ is 1.753×10^{-14}, while Duane's value in effect has coefficient 1.757, the difference being a little less than ¼ per cent. and the error on the side toward the lower values that some other observers have obtained. The gravitation constant from (12*b*) is 6.683×10^{-4}.

Hypothesis II.—Equations (2, 3) are used with S and E determined by (5*a*, 6*a*). Then M_1, here also taken as for the nucleus, by (7*c*) is 1844.8, for the atom 1845.8. Atomic weight of hydrogen as in I· gives $M = 1831.4$, so $\eta = 1.767 \times 10^7$, and $e = 4.778 \times 10^{-10}$, $h = 6.556 \times 10^{-10}$, $h/e^{4/3} = 1.755 \times 10^{-14}$, and then (10), used this time for the gravitation constant, gives $\gamma = 6.696 \times 10^{-8}$.

It seems thus quite possible that some of the equations here proposed foreshadow theoretical results of considerable directness, of a character as required for completion of the theory as it now stands.

THE UNIVERSITY OF CHICAGO,
February 19, 1922.

THE RATIO OF THE TWO ELEMENTARY CHARGES.

By F. W. Loomis.

Synopsis.

Since the oil drops in Millikan's experiments were exactly neutral, ± a small integral number of electronic charges, to 1/1000 of an electron, and since they contained as many as 4×10^{14} protons and nearly the same number of electrons, it follows that *the magnitudes of the charges on protons and electrons are equal to one part in 4×10^{17}.*

In recent years and particularly since the work of Aston it has become generally accepted that all matter is made up of protons and electrons. It is usually taken for granted that the charge on the electron is the negative of that on the proton, but the exactness of this relation is rarely discussed.

Some information can be obtained from positive rays. Aston[1] has found that the positively charged atom of hydrogen, *i.e.*, the proton, shows a deflection corresponding to $m/e = 1.008$ (in units of atomic weight and electronic charge). Since it is a pure element and its chemical atomic weight is 1.008, the magnitude of the charge is found to be equal to that of the electron within the accuracy of Aston's measurements, or 1/10 of 1 per cent. This accuracy is sufficient to establish that the number of protons in a "neutral" atom is equal to the number of electrons, including of course those in the nucleus. Hence it is possible that a more precise measurement of the ratio of the charges might be made by measuring the deflectability of the "neutral" atom; though there would be difficulties due to the confusion of the trace of the "neutral" particles with the darkening caused by the light from the discharge tube.

But much the most precise value of this ratio can be deduced from Millikan's oil-drop experiments.[2] Millikan measured the net charge on oil drops charged in several ways with from 1 to 136 electrons and having masses up to 7×10^{-10} grams. He found that, within 1/10 of 1 per cent., the charge on these drops was always an integral multiple of $e = 4.774 \times 10^{-10}$ esu. Now, since there are about 6×10^{23} protons in a gram of matter, these drops contained 4×10^{14} protons and very nearly the same number of electrons. Hence, since each drop, whatever number of protons it contained, could be made exactly neutral within 1/1000 of the electronic charge, it follows that the ratio of the average charge on a proton to the average charge on an electron is equal to -1 to one part in $1000 \times 4 \times 10^{14}$, *i.e.*, to $-1 \pm 2.5 \times 10^{-18}$. Moreover it would seem a highly improbable coincidence if the charges of protons or electrons should vary among different classes, being different say, in carbon from in hydrogen, or if the charge of the peripheral electrons should differ from those in the K ring or the nucleus, yet in such a way that the average charge on the proton came out exactly equal to the average charge on the electron. So that this experiment may also be considered a precise confirmation of the relativity law of the invariance of electric charge.[1]

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[1] Aston, Phil. Mag., 38 (1919), p. 317.

[2] Millikan, Phil. Mag., 34 (1917), p. 1. The Electron, p. 109.

Probably no physical constant is more accurately known than this ratio. The precision of the measurement arises, somewhat as in interference measurements, from the fact that one is able to compare the charge on a large and necessarily integral number (4×10^{14}) of protons with a similar number of electrons to a precision of 1/1000 of a single charge. Millikan[2] considered the evidence that his experiments afforded on the equality of positive and negative elementary charges. But, writing at a time when Aston's work had not yet identified the universal atom of positive electricity, or proton, and when it was natural to think in terms of a single substance theory of electricity, he merely stated that the positive and negative charges acquired by his drops were all integral multiples of e, and hence "the mean value of the positive electron agrees with the mean value of the negative electron to within less than 1 part in 2000." He was not then in a position to count up the total number of positive and negative elementary charges and state that they were equal to within one part in 4×10^{17}.

It is at present most convenient to think of matter, or electricity, as made up of two fundamental entities, corresponding to protons and electrons. But the exactness of this simple relation between them, analogous to that between inertia and gravitation, is convincing evidence of an underlying unity.

All this does not in any way affect the theory which attributes gravitation to a slight excess in the attraction between charges of opposite sign over the repulsion between charges of the same sign. Which theory, in view of the now recognized identity between electricity and matter, is really not an explanation of gravity at all, but merely an unexceptionable statement that the net force between particles is the sum of the electric and gravitational forces. Even the precision of Millikan's measurements is not enough to detect this excess gravitational force, as one can see without computations; for the effect to be expected is essentially the *gravitational* attraction between the oil drop and the electrons which are driven around from one condenser plate to the other when the electric field is put on. Obviously this is quite beyond the range of Millikan's measurements, which would have to be accurate to one part in 10^{40} to show it.

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[1] Thus, if the velocities of extra-nuclear electrons can be calculated from X-ray data by the Bohr theory, it follows from the fact that the above phenomenon is observed both with oil and mercury drops that, if the charge is proportional to $(1 - v^2/c^2)^n$, then $|n| < 10^{-14}$; or if the charge is expressible as a power series in v/c, then the first term which can have a coefficient as great as 0.001 is the 48th. Still more exact statements can be inferred from any of the usual assumptions about the velocities of nuclear electrons.

[2] Millikan, The Electron, pp. 80–83.

New York University.

RADIATION FROM A GROUP OF ELECTRONS.

By Leigh Page.

Synopsis.

Electric Intensity and Radiation Flux at a Great Distance from a Group of Electrons.—(1) The *general equation* for the intensity is obtained from the field equations of classical electrodynamics by expanding the retarded expression for the intensity due to a point charge:

$$E = \frac{1}{4\pi R c^2}\left[\left\{\frac{d}{dt}(\Sigma e v) + \frac{1}{c}\frac{d^2}{dt^2}(\Sigma e r\cdot M v)\cdots + \frac{1}{(n-1)!c^{n-1}}\frac{d^n}{dt^n}(\Sigma e r\cdot M^{n-1} v) + \cdots\right\}\times M\right]\times M,$$

where R is the distance from a fixed point in the group, r is the position vector of each electron, v its velocity, and M a unit vector in the direction of R. The Poynting flux is merely cE^2. The terms in the series correspond to successive orders of radiation. The general condition for the absence of the nth order of radiation is evidently that $\Sigma e r\cdot M^{n-1} v =$ constant. (2) *For a ring of evenly spaced electrons*, the radiation of all orders less than k, the number of electrons, vanishes; but the radiation of order k does not. In fact $R_k = C_k \beta^{2(k-1)} R_1$, where β is the speed relative to that of light and C_k is a constant which increases rapidly with k, so that for most atoms the higher order radiation from a ring with a number of electrons should be even greater than the radiation from the single electron of the hydrogen atom. Only in the case of a continuous distribution of electricity along the ring do all orders vanish.

Radiationless orbits of Bohr's atomic theory are seen to be in definite conflict with classical electrodynamics. Even the rotation of an asymmetrical positive nucleus would not neutralize the radiation from the hydrogen electron. Therefore, the advisability of seeking some other interpretation of the numerical relationships established by the theory is suggested.

CLASSICAL electrodynamics requires an irreversible radiation of energy from a solitary electron whenever it is accelerated. If, however, a number of electrons at distances from one another small compared to the wave-length emitted are accelerated, the radiations from the individual electrons may interfere in such a way as to annul the first order radiation from the group. This is the case when two or more evenly spaced electrons revolve in a single circular orbit. When the velocities of the electrons are high, however, the radiation of lowest order which does not vanish may be quite comparable with the first order radiation which would be emitted if all the electrons save one were removed. Therefore it has seemed worth while to investigate the higher order radiation from a group of electrons as required by the classical electrodynamics.

Choose as origin some point O in the group of electrons. Describe about O a sphere of radius R very large compared to the greatest distance between electrons in the group. Let $\boldsymbol{c}$ be a vector equal in magnitude to the velocity of light, and having a direction from O toward a point P on the surface of the sphere. The Poynting flux at P is

$$\boldsymbol{s} = c(\boldsymbol{E} \times \boldsymbol{H}).$$

But

$$\boldsymbol{H} = \frac{1}{c}(\boldsymbol{c} \times \boldsymbol{E}),$$

and, as both $\boldsymbol{E}$ and $\boldsymbol{H}$ are at right angles to $\boldsymbol{c}$,

$$\boldsymbol{s} = cE^2. \tag{1}$$

The retarded electric intensity at a distance R from an electron[1] is

$$\boldsymbol{E} = \frac{e}{4\pi R^2 k^2 c\left(1 - \frac{\boldsymbol{c}\cdot\boldsymbol{v}}{c^2}\right)^3}\left[(\boldsymbol{c} - \boldsymbol{v}) + \frac{Rk^2}{c^3}\{\boldsymbol{f} \times (\boldsymbol{c} - \boldsymbol{v})\} \times \boldsymbol{c}\right]$$

in Heaviside-Lorentz rational units, where $\boldsymbol{v}$ is the velocity of the electron, $\boldsymbol{f}$ its acceleration, and $k^2 \equiv 1 - \beta^2$, where $\beta \equiv v/c$. By making R great enough, the first term can be made as small as desired compared to the second, and hence at P

$$\boldsymbol{E} = \frac{e}{4\pi Rc^4\left(1 - \frac{\boldsymbol{c}\cdot\boldsymbol{v}}{c^2}\right)^3}\{\boldsymbol{f} \times (\boldsymbol{c} - \boldsymbol{v})\} \times \boldsymbol{c}. \tag{2}$$

Let $\boldsymbol{r}$ be the position vector of an electron in the group relative to the origin O at the time 0. Denote by $\boldsymbol{M}$ a unit vector in the direction of $\boldsymbol{c}$. Let $\boldsymbol{r}_e$ be the position vector of the electron at the time $\boldsymbol{r}_e\cdot\boldsymbol{M}/c$. Then $\boldsymbol{r}_e$ specifies the *effective position* of the electron. The radiations emitted by all the electrons when in their effective positions will reach P at the same time R/c. The electric intensity involved in this radiation will now be calculated.

Replacing $\boldsymbol{c}$ in (2) by $c\boldsymbol{M}$, and expanding, the electric intensity at P due to a single electron can be put in the form

$$\boldsymbol{E} = \frac{e}{4\pi Rc^2}\left[\left\{\frac{\boldsymbol{f}_e}{(1 - \boldsymbol{\beta}_e\cdot\boldsymbol{M})^2} + \frac{\boldsymbol{f}_e\cdot\boldsymbol{M}}{c}\frac{\boldsymbol{v}_e}{(1 - \boldsymbol{\beta}_e\cdot\boldsymbol{M})^3}\right\} \times \boldsymbol{M}\right] \times \boldsymbol{M}$$

$$= \frac{e}{4\pi Rc^2}\left[\left\{\frac{1}{1 - \boldsymbol{\beta}_e\cdot\boldsymbol{M}}\frac{d}{dt_e}\left(\frac{\boldsymbol{v}_e}{1 - \boldsymbol{\beta}_e\cdot\boldsymbol{M}}\right)\right\} \times \boldsymbol{M}\right] \times \boldsymbol{M}.$$

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[1] See the author's "Introduction to Electrodynamics," p. 29, or Abraham, "Theorie der Electrizität," Vol. II., p. 99.

Now,

$$t_e = \frac{r_e \cdot M}{c},$$

and after a time dt has elapsed at O (Fig. 1),

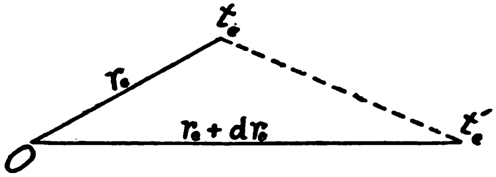

Fig. 1.

$$t_e' = dt + \frac{r_e \cdot M}{c} + \beta_e \cdot M dt_e.$$

Hence

$$\begin{aligned} dt_e &\equiv t_e' - t_e \\ &= dt + \beta_e \cdot M dt_e, \end{aligned}$$

or

$$\frac{1}{1 - \beta_e \cdot M} \frac{d}{dt_e} = \frac{d}{dt} \,. \tag{3}$$

Therefore

$$\begin{aligned} E &= \frac{e}{4\pi R c^2}\left[\left\{\frac{d}{dt}\left(\frac{v_e}{1 - \beta_e \cdot M}\right)\right\} \times M\right] \times M \\ &= \frac{e}{4\pi R c^2}\left[\left\{\frac{d}{dt}\left(\frac{1}{1 - \beta_e \cdot M}\frac{dr_e}{dt_e}\right)\right\} \times M\right] \times M \\ &= \frac{e}{4\pi R c^2}\left[\frac{d^2 r_e}{dt^2} \times M\right] \times M. \end{aligned} \tag{4}$$

Put

$$\tau = \frac{r \cdot M}{c}, \qquad \tau_e = \frac{r_e \cdot M}{c} \,.$$

Then

$$r_e = r + v\tau_e + \frac{1}{2}\dot{v}\tau_e^2 \cdots + \frac{1}{(n-1)!} v^{(n-2)}\tau_e^{n-1} \cdots \tag{5}$$

and

$$\begin{aligned} \tau_e &= \tau + \dot{\tau}\tau_e + \frac{1}{2}\ddot{\tau}\tau_e^2 \cdots + \frac{1}{(n-1)!}\tau^{(n-1)}\tau_e^{n-1} \cdots \\ \tau_e^2 &= \tau^2 + \dot{\overline{\tau^2}}\,\tau_e + \frac{1}{2}\ddot{\overline{\tau^2}}\,\tau_e^2 \cdots + \frac{1}{(n-1)!}\tau^{2(n-1)}\tau_e^{n-1} \cdots \\ &\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ \tau_e^m &= \tau^m + \dot{\overline{\tau^m}}\,\tau_e + \frac{1}{2}\ddot{\overline{\tau^m}}\,\tau_e^2 \cdots + \frac{1}{(n-1)!}\tau^{m(n-1)}\tau_e^{n-1} \cdots \end{aligned} \tag{6}$$

The solution of (6) is

$$\tau_e^m = \tau^m + \frac{m}{m+1}\dot{\overline{\tau^{m+1}}} + \frac{m}{2\cdot m+2}\ddot{\overline{\tau^{m+2}}}\cdots +$$

$$\frac{m}{(n-1)!\,m+n-1}\tau^{m+n-1\,(n-1)}\cdots \qquad (7)$$

The correctness of this solution may be proved by mathematical induction. For assume that the solution has this form for the first n terms of τ_e, for the first $n-1$ terms of τ_e^2, and in general for the first $n-m+1$ terms of τ_e^m for all m's less than $n+1$. Then by substituting the assumed terms in (6), the $n-m+2$ term of τ_e^m is found to be

$$\frac{1}{(n-m+1)!}\left[\tau^{m\,(n-m+1)}\tau^{n-m+1} + (n-m)\tau^{m\,(n-m)}\tau^{n-m+1\,(1)} + \text{etc.}\right],$$

which, by Leibnitz's theorem for the kth derivative of the product of two factors, is equal to

$$\frac{1}{(n-m+1)!}\frac{d^{n-m}}{dt^{n-m}}\left[\frac{d}{dt}(\tau^m)\tau^{n-m+1}\right]$$

$$= \frac{m}{(n-m+1)!}\frac{d^{n-m}}{dt^{n-m}}\left[\tau^n\dot{\tau}\right]$$

$$= \frac{m}{(n-m+1)!\,n+1}\tau^{n+1\,(n-m+1)},$$

which is the form predicted by (7) for the $n-m+2$ term.

Now the first term of τ_e is obviously τ. Hence all the terms of all the series are as given by (7).

Substituting in the expression (5) for r_e the values of τ_e^m given by (7), the nth term of r_e is found to be

$$\frac{1}{(n-1)!}\left[v^{(n-2)}\tau^{n-1} + (n-2)v^{(n-3)}\tau^{n-1\,(1)} + \text{etc.}\right]$$

$$= \frac{1}{(n-1)!}\frac{d^{n-2}}{dt^{n-2}}(v\tau^{n-1}).$$

Hence

$$r_e = r + v\tau + \frac{1}{2}\frac{d}{dt}(v\tau^2)\cdots + \frac{1}{(n-1)!}\frac{d^{n-2}}{dt^{n-2}}(v\tau^{n-1})\cdots \qquad (8)$$

and substitution in (4) gives the electric intensity due to a single electron at a great distance R from the group in the direction M. Summing up over all the electrons, and replacing τ by $\mathbf{r}\cdot\mathbf{M}/c$, the total electric intensity at P is seen to be

$$\mathbf{E} = \frac{1}{4\pi Rc^2}\left[\left\{\frac{d}{dt}(\,\Sigma e\mathbf{v}) + \frac{1}{c}\frac{d^2}{dt^2}(\,\Sigma e\mathbf{r}\cdot\mathbf{M}\mathbf{v}) + \frac{1}{2c^2}\frac{d^3}{dt^3}(\,\Sigma\overline{e\mathbf{r}\cdot\mathbf{M}}^2\mathbf{v})\right.\right.$$
$$\left.\left.\cdots + \frac{1}{(n-1)!\,c^{n-1}}\frac{d^n}{dt^n}(\,\Sigma\overline{e\mathbf{r}\cdot\mathbf{M}}^{n-1}\mathbf{v})\cdots\right\}\times\mathbf{M}\right]\times\mathbf{M}. \tag{9}$$

Now (1) shows that the condition for absence of radiation is that $\mathbf{E}$ shall vanish for all directions of $\mathbf{M}$. If the electrons are to remain in a group, and not become separated further and further as time goes on, this condition requires that each of the vector sums enclosed in parentheses in (9) shall remain constant in time. Therefore in scalar notation the conditions for absence of radiation of each order are:

Order of Radiation.	Conditions.	No. of Conditions for Three-dimensional Motion.	No. of Conditions for Two-dimensional Motion.
1st........	$\Sigma e\dot{x}_j$ = const.	3	2
2d.........	$\Sigma ex_a\dot{x}_j$ = const.	9	4
3d.........	$\Sigma ex_ax_b\dot{x}_j$ = const.	18	6
nth........	$\Sigma ex_ax_b\cdots x_{n-1}\dot{x}_j$ = const.	$\frac{3}{2}n(n+1)$	$2n$

where x_1, x_2, x_3 are rectangular coördinates, and the suffixes a, b, $c\cdots$ assume values corresponding to all independent combinations of 1, 2, and 3, j having successfully the values 1, 2, and 3. As Larmor[1] has pointed out, a necessary but not sufficient condition for absence of second order radiation is that the magnetic moment of the group remain constant.

An interesting application of the conditions for absence of radiation can be made to the case of k evenly spaced electrons revolving in a fixed circular orbit with constant speed. The conditions for absence of radiation of the nth order become

$$e\Omega a^n\sum_p \sin^\alpha\ (\theta + P)\cos^\beta\ (\theta + P) = \text{const.}, \tag{10}$$

where Ω is the common angular velocity of the electrons, a the radius of the orbit, α and β any positive integers whose sum is n, θ the angular displacement of the first electron, and

$$P \equiv \frac{2\pi}{k}(p - 1),$$

the summation over the electrons extending from $p = 1$ to $p = k$.

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[1] Phil. Mag., *42*, 595, 1921.

Writing the sine and cosine in exponential form, expanding by the binomial theorem and multiplying, each term in (10) is easily seen to have the form

$$C\sum_{p} e^{i[n-2(s+t)][\theta+P]} = f(\theta)\,\frac{1 - e^{2\pi i[n-2(s+t)]}}{1 - e^{\frac{2\pi}{k} i[n-2(s+t)]}}$$

where s and t are positive integers such that

$$s + t \leqq n,$$

and C is a constant not containing θ.

When $n - 2(s + t)$ is zero, the term reduces to the constant pC, which is not a function of θ and hence does not vary with the time. Otherwise each term vanishes except when $n - 2(s + t)$ is equal to an integral multiple of k. But this cannot occur if n is less than k. Hence *the radiation of all orders less than the number of electrons in the ring vanishes.* Thus, if there are two electrons in the ring, the first order radiation will vanish; if there are eight electrons, radiation of the first seven orders will vanish.

Suppose that the number k of electrons in the ring is even. Then all odd orders of radiation vanish, for $n - 2(s + t)$ cannot equal k for n odd. Similarly, if the number of electrons in the ring is odd, all even orders of radiation less than $2k$ vanish.

If the number of electrons in the ring is infinite, the radiation of all orders vanishes. Hence a continuous ring of electricity of uniform density rotating about its axis of symmetry will not radiate—a well-known result.[1]

The radiation emitted by any specified group of electrons may easily be calculated from (9) and (1). Thus the total radiation of lowest order emitted by a pair of electrons revolving in a circle so as to be always at opposite ends of a diameter, is the second order radiation. In Heaviside-Lorentz rational units, it amounts to

$$R_2 = 9.6\beta^2 R_1, \tag{11}$$

where

$$R_1 \equiv \frac{e^2 f^2}{6\pi c^3}$$

is the first order radiation that would be emitted by one of the two electrons in the absence of the other. Therefore the second order radiation from a pair of electrons is greater than the first order radiation from a single electron traversing the same orbit at the same rate if

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[1] Schott, Phil. Mag., *36*, 255, 1918.

$$\beta > .323.$$

On Bohr's theory of the atom this occurs in the K rings of elements of atomic number greater than 44 (ruthenium). Furthermore, a simple calculation shows that the second order radiation from the pair of electrons in the K rings of elements of atomic number greater than 2 (helium) should be greater than the first order radiation from the single electron in the hydrogen atom when it is in the first Bohr ring.

In general, if k evenly spaced electrons are revolving in a circular orbit, the radiation of the kth order (which is the lowest order which does not vanish) is

$$R = C_k \, \beta^{2(k-1)} R_1,$$

where the numerical constant C_k increases rather rapidly with k, being 9.6 for two electrons and 173 + for four electrons.

The chief object of this paper is to emphasize the inconsistency between Bohr's theory of the atom and classical electrodynamics. In the case of the hydrogen or ionized helium atom, where the theory has been most successful, Bohr requires the single electron to revolve about the nucleus in a circular or elliptical orbit without radiating. Electrodynamics, on the other hand, allows no possibility of orbital motion of a solitary electron without radiation. Even in the case of a number of electrons following one another around the same orbit, the higher order radiation emitted should be greater, in the case of most atoms, than the first order radiation from hydrogen. Now the radiation of energy specified by the Poynting vector is one of the most fundamental properties of classical electrodynamics. Hence it is difficult to see how electrodynamics and Bohr's theory of the atom can ever find a common ground. This raises the question of the advisability of seeking for other than a dynamical interpretation of the numerical relationships which Bohr's theory has been so successful in establishing.

It might be thought that the radiation from the single electron in the hydrogen or ionized helium atom might be annulled by radiation from an symmetrical nucleus rotating at the same rate as the electron. Suppose, for instance, that the hydrogen nucleus consists of two small coincident circular rings of electricity, one positive and the other negative, rotating in opposite senses about their common center, and having charges of such densities that the net charge on the nucleus is one unit of positive electricity. Investigation shows that the asymmetric distribution of charge and the angular velocity of rotation can be chosen so as to satisfy the conditions of each order for absence of radiation from the atom. But the equal quantities of positive and negative electricity which must be distributed asymmetrically on the two rings to annul the radiation of each order become greater and greater as the order increases, as indeed is evident from the fact that the exponent of $\mathbf{r}\cdot\mathbf{M}$ in the terms of (9) increases with the ordinal number of the term. Hence the presence of infinite amounts of both positive and negative electricity within the nucleus would be required in order to make possible the entire annulment of radiation from the atom—a condition which makes the formal solution of the problem of no physical value.

Sloane Physics Laboratory,
Yale University,
Jan. 26, 1922.

ANOTHER ETHER-DRIFT EXPERIMENT.

By Roy J. Kennedy.

Synopsis.

Introduction.—The ether drift experiments heretofore performed seem to have proven the reality of the Lorentz-Fitzgerald contraction, but the explanation of the negative results requires nothing further. The experiment forming the subject of this paper is designed to detect ether drift or to confirm the time transformation between relatively moving systems, which is an essential part of the theory of relativity.

Theory.—Assuming Huyghen's principle and the Lorentz-Fitzgerald contraction it can be shown that the paths of light rays relative to a system are unaffected by its motion or orientation in the medium transmitting the light. The relative phases of two homogeneous beams superposed under large retardation are unaffected by the orientation but not by the velocity of the system. The effect sought in this experiment depends on the velocity change due to the alternate adding and subtracting of the earth's orbital motion and that of the solar system as a whole.

Apparatus and Method.—A delicate optical system is used in which a half-shade analyzer measures the variation with change of phase of component beams, of the position of the plane of polarization of a beam resulting from the superposition of two oppositely circularly polarized ones. The change manifests itself as an unbalancing of a uniform photometric field. The smallest effect to be expected according to the classical ether theory is shown to be several times the least detectable with the experimental arrangements, so that conclusive evidence for or against the relativity principle should be obtained.

Introduction.—The negative results of all experiments devised to detect relative motion between the earth and the ether, which gave rise to the theory of relativity, can be explained without modification of the classical electromagnetic theory if the forces on which the size and shape of rigid bodies depend are assumed to be electrical. For then the Lorentz-Fitzgerald contraction of the experimental apparatus follows necessarily, and nothing further than the contraction is required to account for the absence of any physical effect of motion with the arrangements heretofore used. For this reason the hypothesis of the relativity of time, which is essential to the theory of relativity, appears to be a gratuitous assumption. This paper is an outline of an experiment which is intended to detect ether-motion or, failing that, to establish the validity of the Lorentz-Einstein time transformation. It is being performed by the writer at the Palmer Physical Laboratory.

Apparatus.—The arrangement of apparatus is as shown in Fig. 1. A beam of homogeneous plane-parallel light polarized in a plane inclined at an angle of 45° to that of the paper falls on a Wollaston prism *W* which divides it into two beams of equal intensity and plane polarized in planes at right angles to one another. The one whose plane of polarization is in the plane of the paper passes to the mirror M_1, from which it is reflected to mirror M_2, and thence to a partially silvered mirror M_3. Here it is reflected and superposed on the other ray, which is polarized in a plane at right angles to the paper and passes through M_3. The elliptically polarized beam resulting from this superposition passes through a Fresnel rhomb *R*, so placed as to render it plane polarized, the inclination of the plane of polarization depending on the phase relation between the two beams combining at M_3. From *R* the beam passes between and through the small nicols *NN*, whose principal sections are parallel, through the analyzing nicol *A* and to the eye at *E* by way of the lens system *LL*. The nicols *NN* are fixed in position, while the nicol *A* is rotatable about an axis in the direction of the rays through it, its position being read off a graduated circle. The optical parts are mounted so that temperature changes are compensated for and do not affect the paths of the rays.

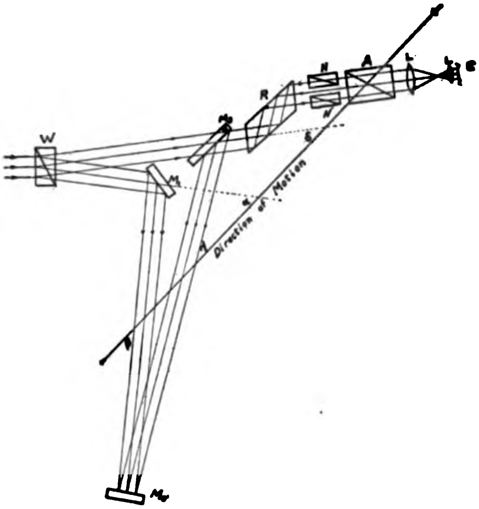

Fig. 1.

Such an arrangement provides a very sensitive measure of any change in relative phase of the two superposed beams. It can be shown that if the plane of polarization of the light emerging from the rhomb *R* makes an angle θ with the planes of the principal sections of the nicols *NN*, and ψ is the angle between the principal sections of *NN* and of *A* when the latter prism is set so that it lets through equal amounts of the light passed through and between NN, then to a small change $\delta\theta$ in θ there corresponds a change in ψ

$$\delta\psi = \frac{2\,\delta\theta}{1 + 3\cos^2\theta}.$$

Since for the greatest sensibility θ must be small (not greater than two or three degrees), $\delta\psi$ will be about half of $\delta\theta$. The light emerging from R may be regarded as the resultant of two oppositely circularly polarized beams; a little consideration will show that its plane will rotate through 180° as the relative phase of the component beams varies through 360° or one wave. With a sufficiently intense source of light the analyzer A can be set accurately to one-hundredth of a degree; that is, a change $\delta\psi = 0.01$ can be detected. Therefore a change in the phase ϕ of

$$\delta\phi = \frac{2 \times .01^\circ}{180^\circ} = \frac{1}{9000} \text{ wave}$$

can be detected. An ordinary Michelson or Fabry and Perot interferometer could be used but for their low sensibility.

Theory.—Assuming the existence of an ether with respect to which the surface of the earth and the apparatus are in motion with a velocity v, and the Lorentz-Fitzgerald contraction which reduces dimensions in the direction of motion in the ratio $\sqrt{1 - \frac{v^2}{c^2}} : 1$ (where c is the velocity of light in ether), the theory of the experiment is as follows:

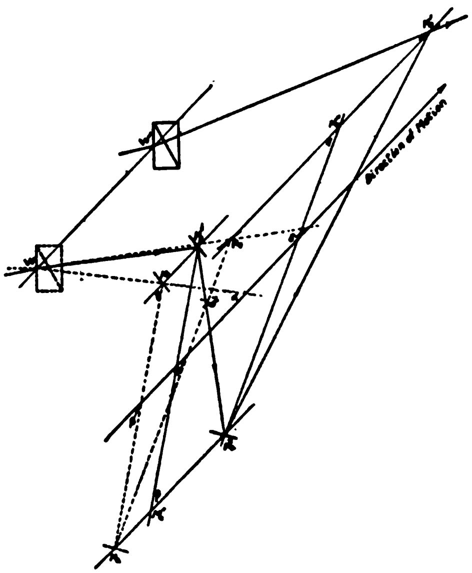

Fig. 2.

In Fig. 2 the dotted broken lines, $WM_1M_1M_3$ and WM_3 represent the paths of the two beams relative to the apparatus. The full lines $WM_1'M_2'M_3'$ and $W'M_3'$ are the paths as referred to the ether. The dotted line sketch of the Wollaston prism and the mirrors shows them in the position occupied at the instant the lower beam leaves the prism. The full line sketches show the positions of the mirrors as they are successively reached by the wave front, and of the prism at the instant of starting of the upper train which will combine at M_3' with the lower. M_2'' is position of mirror M_2 at the instant when the wave front starts from M_1' and M_3'' is that of the mirror M_3 when the wave front leaves M_2'.

Let the lengths WM_1 equal l_1, M_1M_2 equal l_2, M_2M_3 equal l_3, and WM_3 equal l_4, these being the values which would be measured by an observer stationary in the ether — the "contracted" values. Let the direction of motion makes angles α with WM_1, β with M_1M_2, γ with M_2M_3 and δ with WM_3. Consider first the ray from the prism to the mirror M_1. Due to the motion of the system, its actual path in the ether will be along WM_1' instead of WM_1, and if the time required for the light to travel this distance is t_1, we have from the geometry of the figure,

$$\begin{aligned} c^2t_1^2 &= \overline{WM_1}^2 + \overline{M_1M_1'}^2 - 2\,\overline{WM_1}\;\overline{M_1M_1'}\cos < WM_1M_1' \\ &= l_1^2 + v^2t_1^2 - 2\,l_1vt_1\cos(\pi - \alpha) \\ &= l_1^2 + v^2t_1^2 + 2l_1vt_1\cos\alpha. \end{aligned}$$

After reflection at M_1' the light travels to M_2' in time t_2 a distance whose square is

$$\begin{aligned} c^2t_2^2 = \overline{M_1'M_2'}^2 &= \overline{M_1'M_2''}^2 + \overline{M_2''M_2'}^2 - 2\,\overline{M_1'M_2''}\;\overline{M_2''M_2'}\cos\beta \\ &= l_2^2 + v^2t_2^2 - 2\,l_2vt_2\cos\beta. \end{aligned}$$

After reflection at M_2' the ray proceeds to M_3' in time t_3 a distance whose square is

$$\begin{aligned} c^2t_3^2 = \overline{M_2'M_3'}^2 &= \overline{M_2'M_3''}^2 + \overline{M_3''M_3'}^2 - 2\,\overline{M_2'M_3''}\;\overline{M_3''M_3'}\cos(\pi-\gamma) \\ &= l_3^2 + vt_3^2 + 2\,l_3vt_3\cos\gamma. \end{aligned}$$

At M_3' the ray combines with one directly from W' which has gone in time t_4 a distance given by

$$c^2t_4^2 = \overline{W'M_3'}^2 = l_4^2 + v^2t_4^2 + 2\,l_4vt_4\cos\delta.$$

Solving these four equations and rejecting one physically meaningless solution of each we obtain

$$t_1 = \frac{l_1}{c^2 - v^2}\left(v\cos\alpha + c\sqrt{1 - \frac{v^2}{c^2}\sin^2\alpha}\right),$$

$$t_2 = \frac{l_2}{c^2 - v^2}\left(- v \cos \beta + c\sqrt{1 - \frac{v^2}{c^2}\sin^2 \beta}\right),$$

$$t_3 = \frac{l_3}{c^2 - v^2}\left(v \cos \gamma + c\sqrt{1 - \frac{v^2}{c^2}\sin^2 \gamma}\right),$$

$$t_4 = \frac{l_4}{c^2 - v^2}\left(v \cos \delta + c\sqrt{1 - \frac{v^2}{c^2}\sin^2 \delta}\right).$$

If we represent by primed letters the distances between pairs of points in the system when it is at rest (which are the distances actually obtained by measurement by an observer moving with the system)then any length $l = l'\sqrt{1 - (v^2/c^2)\cos^2 \omega}$ where ω is the angle between direction of the motion and the line joining the two points. For the component l_y of the length perpendicular to the motion is unaffected while the parallel component l_x is contracted to $\sqrt{1 - (v^2/c^2)}$ times its value when stationary, and

$$l = \sqrt{l_y^2 + l_x^2} = \sqrt{(l' \sin \omega)^2 + \left(l'\sqrt{1 - \frac{v^2}{c^2}\cos \omega}\right)^2}$$

$$= l'\sqrt{\sin^2 \omega + \cos^2 \omega - \frac{v^2}{c^2}\cos^2 \omega}$$

$$= l'\sqrt{1 - \frac{v^2}{c^2}\cos^2 \omega}.$$

Therefore

$$l_1 = l_1'\sqrt{1 - \frac{v^2}{c^2}\cos^2\alpha}, \qquad l_3 = l_3'\sqrt{1 - \frac{v^2}{c^2}\cos^2\gamma},$$

$$l_2 = l_2'\sqrt{1 - \frac{v^2}{c^2}\cos^2\beta}, \qquad l_4 = l_4'\sqrt{1 - \frac{v^2}{c^2}\cos^2\delta}.$$

Substituting these values in formulas (1)

$$t_1 = \frac{l_1'}{c^2 - v^2}\left(v \cos \alpha\sqrt{1 - \frac{v^2}{c^2}\cos^2\alpha}\right.$$

$$\left. + c\sqrt{1 - \frac{v^2}{c^2}\sin^2\alpha - \frac{v^2}{c^2}\cos^2\alpha + \frac{v^4}{c^4}\sin^2\alpha \cos^2\alpha}\right)$$

$$= \frac{l_1'}{c^2 - v^2}\left(v \cos \alpha\sqrt{1 - \frac{v^2}{c^2}\cos^2\alpha} + c\sqrt{1 - \frac{v^2}{c^2}}\right),$$

neglecting the fourth order term $(u^4/c^4)\sin^2\alpha \cos^2\alpha$. Similar relations hold for t_2, t_3 and t_4 so that the retardation of the reflected ray relative to the direct ray may be written

$T = t_1 + t_2 + t_3 - t_4$

$$
\begin{aligned}
= \frac{1}{c^2 - v^2}\bigg[v\bigg(& l_1'\sqrt{1 - \frac{v^2}{c^2}\cos^2\alpha}\cos\alpha - l_2'\sqrt{1 - \frac{v^2}{c^2}\cos^2\beta}\cos\beta \\
& + l_3'\sqrt{1 - \frac{v^2}{c^2}\cos^2\gamma}\cos\gamma - l_4'\sqrt{1 - \frac{v^2}{c^2}\cos^2\delta}\cos\delta\bigg) \\
& + c\sqrt{1 - \frac{v^2}{c^2}}\,(l_1' + l_2' + l_3' - l_4')\bigg].
\end{aligned}
$$

The coefficient of v in this expression is zero, since it is the algebraic sum of the projections of the sides of a closed figure on a line (the direction of motion). Hence

$$
\begin{aligned}
T &= \frac{c\sqrt{1 - \frac{v^2}{c^2}}\,(l_1' + l_2' + l_3' - l_4')}{c^2 - v^2}, \\
&= \frac{1}{c\sqrt{1 - \frac{v^2}{c^2}}}(l_1' + l_2' + l_3' - l_4').
\end{aligned}
$$

As would be expected, this retardation is not a function of the orientation of the system; this is indicated by the absence of α, β, γ and δ from the expression for T. Its value does, however, depend on the velocity of the system. For another value v' of the velocity, the new retardation

$$
T' = \frac{1}{c\sqrt{1 - \frac{v'^2}{c^2}}}(l_1' + l_2' + l_3' - l_4')
$$

and

$$
\begin{aligned}
T - T' &= \left(\frac{1}{\sqrt{1 - \frac{v^2}{c^2}}} - \frac{1}{\sqrt{1 - \frac{v'^2}{c^2}}}\right)\frac{l_1' + l_2' + l_3' - l_4'}{c} \\
&= \left(1 + \frac{1}{2}\frac{v^2}{c^2} + \frac{3}{8}\frac{v^4}{e^4}\cdots\cdots - 1 - \frac{1}{2}\frac{v'^2}{c^2} - \frac{3}{8}\frac{v'^4}{c^4}\cdots\cdots\right) \\
&\qquad \frac{l_1' + l_2' + l_3' - l_4'}{c} \\
&= \frac{v^2 - v'^2}{2c^2}\left(l_1' + l_2' + l_3' - l_4'\right)
\end{aligned}
$$

to a very close approximation. This quantity is the difference between the time-retardations for the two velocities. The change $\delta\phi$ in the number of waves corresponding to this time is $T—T'$ multiplied by the frequency of the light employed. But the frequency equals c/λ, so that

$$
\delta\phi = \frac{c}{\lambda}\left(T - T'\right) = \frac{v^2 - v'^2}{2c^2}\left(\frac{l_1' + l_2' + l_3' - l_4'}{\lambda}\right).
$$

Up to the last step, nothing in the argument is contrary to the relativity hypothesis if the times T and T' be taken as determined by an observer stationary in the ether. The departure is in assuming λ to be the same for both velocities, v and v'. For according to the relativity time transformation, the indication of a clock in one system during the interval between two events, as observed from the other system, is equal to $\sqrt{1 - (v^2/c^2)}$ times the indication of a clock in the latter between the same events. To an observer stationary in the ether, then, any time indicator in the apparatus of this experiment should run slow in the above ratio. A luminous emitter is a form of clock of which the indication is expressed as a certain number of waves. If its rate decreases to $\sqrt{1 - (v^2/c^2)}$ times its rest value, the wave length corresponding to a given spectral line will increase in the inverse ratio; *i.e.*, if λ_0 be the wave length corresponding to the line when the system is at rest in the ether, the wave length for a velocity v will be $\dfrac{\lambda_0}{\sqrt{1 - \dfrac{v^2}{c^2}}}$.

If this value is substituted in the expression for the retardation in waves (= T times the frequency) we have

$$\frac{Tc}{\lambda} = \frac{c}{\dfrac{\lambda_0}{\sqrt{1 - \dfrac{v^2}{c^2}}}\, c\sqrt{1 - \dfrac{v^2}{c^2}}}\,(l_1' + l_2' + l_3' - l_4')$$

$$= \frac{l_1' + l_2' + l_3' - l_4'}{\lambda_0}.$$

This is quite independent of v and would predict a negative result for the experiment.

The effect to be expected if the frequency is not affected by the motion is well within the range of the apparatus. It has been found possible to secure interference with a retardation (equal to $(l_1' + l_2' + l_3' - l_4')/\lambda$) of over a million waves, so it is probable that half that retardation will be found feasible. It was shown above that a value of $\delta\phi$ equal to $\frac{1}{5000}$ wave could be detected under good conditions. As a conservative estimate let us assume that about $\frac{1}{2000}$ wave is the least value under the less favorable condition of high retardation that will obtain in the experiment. The least difference of the squares of the velocities (in miles per second) detectable will then be

$$V^2 - V'^2 = \frac{2c^2\,\delta\phi}{\left(\dfrac{l_1' + l_2' + l_3' - l_4'}{\lambda}\right)} = \frac{2 \times (186{,}000)^2 \times .0005}{500{,}000}.$$

$$= 69, \text{ approximately.}$$

This is about four times the value of the diurnal difference of squares if the earth is supposed to have a velocity with respect to the ether equal to its orbital velocity merely (the least that can be ascribed to it). If the velocity is twice this at some time of the year the effect would be just observable. The yearly variation due to the motion of the solar system as a whole should be many times as great. If this latter speed is no greater than that towards the constellation Hercules — which is supposed to be the average velocity with respect to the whole sidereal system — which has a maximum component in the earth's orbital plane of slightly more than six miles per second, the maximum and minimum values of the velocity are $18 + 6$ and $18 - 6$, so that $V^2 - V'^2 = 24^2 - 12^2 = 432$. It is quite probable that the actual velocity is much greater.

If the experiment does show relative motion between earth and ether, it will be possible to determine the absolute value of it. For the difference between the first powers of the two velocities will be known from the earth's orbital and rotational velocities, and the experiment will give the difference between their squares, thus supplying the two equations necessary to determine two unknowns. If no positive effect is obtained, the relativity time transformation between a system stationary in the ether and one moving with respect to it would seem to be confirmed.

Palmer Physical Laboratory,
Princeton University,
February, 1922.

NOTE ON THE LORENTZIAN ELECTRON.

By I. Maizlish.

Synopsis.

The Effect of a Uniform Dilation of the Lorentzian Electron.

Assuming that, in addition to the contraction *in the line of motion*, the Lorentzian electron experiences a *uniform* expansion proportional to a function, $\lambda(\beta)$, of the ratio of its velocity to that of light, the author derives general expressions for the longitudinal and transverse momenta and masses, and shows that a dilation equal to

$$\frac{G\beta}{G\beta+\delta\sqrt{1-\beta^2}}$$

would leave the longitudinal mass unaltered whatever G and δ may be. But if *both* masses are to be identical with those given by the formulæ of Lorentz, then there can be no uniform dilation of the electron.

1. It is usually assumed that the Lorentzian electron suffers only a contraction *in the line of motion*. Suppose that, in addition to this contraction, the electron experiences a *uniform* expansion (or contraction) of amount $G(a, \sigma)\lambda(\beta)$; where $\beta \equiv (v/c)$, $v =$ velocity of the electron, $c =$ velocity of light, $\lambda(\beta)$ is a function of β, a is the radius of the electron, σ is an arbitrary constant (*e.g.*, the electronic charge), and $G(a, \sigma)$ is an arbitrary function of a and σ. Let it be required to find that function, $\lambda(\beta)$, of β which will give the Lorentzian masses for *all* velocities.

2. Let symbols without subscript refer to the moving system, and those with subscript $_1$ to the corresponding static system. Then

$$\begin{aligned} x &= G(a, \sigma)\lambda(\beta)S^{1/2}\cdot x_1, \\ y &= G(a, \sigma)\lambda(\beta)y_1, \\ z &= G(a, \sigma)\lambda(\beta)z_1, \end{aligned} \tag{1}$$

where $S \equiv 1 - \beta^2$.

We also have the relation:[1]

$$\frac{\partial}{\partial t} = -v\frac{\partial}{\partial x}. \tag{2}$$

---

[1] O. W. Richardson, The Electron Theory of Matter, second edition (1916), p. 218. The electron is supposed to move in the direction of the X-axis. For the sake of completeness I have included some equations which are not necessary for the argument.

From equations (1) we get immediately:

$$\begin{aligned} \frac{\partial}{\partial x} &= \frac{1}{G\cdot\lambda(\beta)S^{1/2}}\cdot\frac{\partial}{\partial x_1}, \\ \frac{\partial}{\partial y} &= \frac{1}{G\cdot\lambda(\beta)}\cdot\frac{\partial}{\partial y_1}, \\ \frac{\partial}{\partial z} &= \frac{1}{G\cdot\lambda(\beta)}\cdot\frac{\partial}{\partial z_1}, \end{aligned} \tag{3}$$

where $G \equiv G(a, \sigma)$. The equations which we will make use of are:

$$\nabla^2\varphi - \frac{1}{c^2}\frac{\partial^2\varphi}{\partial t^2} = -\rho, \tag{4}$$

$$\nabla^2 U - \frac{1}{c^2}\frac{\partial^2 U}{\partial t^2} = -\rho\frac{v}{c}, \tag{5}$$

$$E = -\frac{1}{c}\frac{\partial U}{\partial t} - \nabla\varphi, \tag{6}$$

and

$$H = \nabla \times U. \tag{7}$$

If we make use of equation (2), equation (4) may be put under the form:

$$S\left(\frac{\partial^2\varphi}{\partial x^2}\right) + \frac{\partial^2\varphi}{\partial y^2} + \frac{\partial^2\varphi}{\partial z^2} = -\rho. \tag{8}$$

Let us now change (8) to "static coördinates." From equations (3), it is easily seen that (8) becomes

$$\frac{1}{G^2\lambda^2(\beta)}\cdot\frac{\partial^2\varphi}{\partial x_1^2} + \frac{1}{G^2\lambda^2(\beta)}\frac{\partial^2\varphi}{\partial y_1^2} + \frac{1}{G^2\lambda^2(\beta)}\frac{\partial^2\varphi}{\partial z_1^2} = -\rho, \tag{9}$$

that is,

$$\frac{1}{G^2\lambda^2(\beta)}\left[\frac{\partial^2\varphi}{\partial x_1^2} + \frac{\partial^2\varphi}{\partial y_1^2} + \frac{\partial^2\varphi}{\partial z_1^2}\right] = -\rho. \tag{10}$$

The invariance of the electric charge gives:

$$\rho_1 = S^{1/2}G^3\cdot\lambda^3(\beta)\cdot\rho. \tag{11}$$

Equation (10) may now be written as

$$\frac{\partial^2\varphi}{\partial x_1^2} + \frac{\partial^2\varphi}{\partial y_1^2} + \frac{\partial^2\varphi}{\partial z_1^2} = -\frac{\rho_1}{S^{1/2}G\cdot\lambda(\beta)}. \tag{12}$$

But in the static system φ_1 satisfies the relation

$$\frac{\partial^2\varphi_1}{\partial x_1^2} + \frac{\partial^2\varphi_1}{\partial y_1^2} + \frac{\partial^2\varphi_1}{\partial z_1^2} = -\rho_1. \tag{13}$$

Hence, from equations (12) and (13), we conclude that

$$\varphi = \frac{1}{S^{1/2}\cdot G\cdot\lambda(\beta)}\cdot\varphi_1. \tag{14}$$

From equations (4) and (5) it is seen that

$$U = \beta\varphi. \tag{15}$$

3. From equations (6), (7), and (15), remembering that

$$U_y = U_z = 0; \quad U_x = \beta\varphi,$$

we get the following relations:

$$\begin{aligned} E_x &= -\frac{1}{G^2\cdot\lambda^2(\beta)}\cdot\frac{\partial\varphi_1}{\partial x_1}, \\ E_y &= -\frac{1}{S^{1/2}\cdot G^2\cdot\lambda^2(\beta)}\cdot\frac{\partial\varphi_1}{\partial y_1}, \\ E_z &= -\frac{1}{S^{1/2}\cdot G^2\cdot\lambda^2(\beta)}\cdot\frac{\partial\varphi_1}{\partial z_1}, \end{aligned} \tag{16}$$

and

$$\begin{aligned} H_x &= 0, \\ H_y &= \frac{\beta}{S^{1/2}\cdot G^2\cdot\lambda^2(\beta)}\cdot\frac{\partial\varphi_1}{\partial z_1}, \\ H_z &= -\frac{\beta}{S^{1/2}\cdot G^2\cdot\lambda^2(\beta)}\cdot\frac{\partial\varphi_1}{\partial y_1}. \end{aligned} \tag{17}$$

The momentum per unit volume is

$$\frac{1}{c}\,\mathbf{E}\times\mathbf{H}. \tag{18}$$

Therefore, the components of the momentum per unit volume are:

$$\begin{aligned} g_x &= \frac{\beta}{cSG^4\lambda^4(\beta)}\left[\left(\frac{\partial\varphi_1}{\partial y_1}\right)^2+\left(\frac{\partial\varphi_1}{\partial z_1}\right)^2\right], \\ g_y &= \frac{-\beta}{cS^{1/2}\cdot G^4\lambda^4(\beta)}\left[\frac{\partial\varphi_1}{\partial x_1}\cdot\frac{\partial\varphi_1}{\partial y_1}\right], \\ g_z &= -\frac{\beta}{S^{1/2}\cdot c\cdot G^4\lambda^4(\beta)}\left[\frac{\partial\varphi_1}{\partial x_1}\cdot\frac{\partial\varphi_1}{\partial z_1}\right], \end{aligned} \tag{19}$$

with

$$dxdydz = d\tau = \sqrt{S}\cdot G^3\cdot\lambda^3(\beta)d\tau_1 = \sqrt{S}\cdot G^3\cdot\lambda^3(\beta)dx_1dy_1dz_1.$$

Hence, considering only the X-component of the total momentum, we have

$$S_x = \frac{\beta}{c\cdot G\cdot\lambda(\beta)\sqrt{1-\beta^2}}\iiint\left[\left(\frac{\partial\varphi_1}{\partial y_1}\right)^2+\left(\frac{\partial\varphi_1}{\partial z_1}\right)^2\right]d\tau_1. \tag{20}$$

The value of

$$\iiint\left[\left(\frac{\partial\varphi_1}{\partial y_1}\right)^2+\left(\frac{\partial\varphi_1}{\partial z_1}\right)^2\right]d\tau_1$$

is known[1] to be $(e^2/6\pi a)$. Therefore,

$$S_x = \frac{\beta \cdot e^2}{6\pi ac \cdot G \cdot \lambda(\beta) \sqrt{1-\beta^2}}. \tag{21}$$

4. *To Find the Longitudinal and Transverse Masses.*—If F_x be the force in the direction of motion, m_L the longitudinal mass, and m_t the transverse mass, we have

$$F_x = \frac{\partial S_x}{\partial t}, \text{ by definition;}$$

$$= \frac{e^2 \ddot{x}_1}{6\pi ac^2 \sqrt{1-\beta^2}} \left[\frac{1}{G \cdot S \cdot \lambda(\beta)} - \frac{\beta \lambda'(\beta)}{G \cdot \lambda^2(\beta)} \right],$$

by substitution from (21). The longitudinal mass, however, is defined by

$$F_x = m_L \ddot{x}_1.$$

Therefore,

$$m_L = \frac{e^2}{6\pi ac^2 \sqrt{1-\beta^2}} \left[\frac{1}{G \cdot S \cdot \lambda(\beta)} - \frac{\beta \cdot \lambda'(\beta)}{G \cdot \lambda^2(\beta)} \right]. \tag{22}$$

The transverse mass is given by

$$m_t = \frac{S_x}{v} = \frac{S_x}{\beta c}$$

$$= \frac{e^2}{6\pi ac^2 \cdot G \cdot \lambda(\beta) \sqrt{1-\beta^2}}. \tag{23}$$

But now, the expressions for the masses given by Lorentz are:

$$M_L = \frac{e^2}{6\pi ac^2 (1-\beta^2)^{3/2}}, \tag{24}$$

$$M_t = \frac{e^2}{6\pi ac^2 \sqrt{1-\beta^2}}. \tag{25}$$

Let us now determine $\lambda(\beta)$ so that we have always

$$M_L = m_L.$$

From equations (22) and (24) we get the following relation from which we are to determine $\lambda(\beta)$:

$$G \cdot \lambda^2(\beta) = \lambda(\beta) - \beta(1-\beta^2)\lambda'(\beta). \tag{26}$$

Let $\xi \equiv \lambda(\beta)$. Then,

$$G\xi^2 = \xi - \beta(1-\beta^2)\frac{d\xi}{d\beta};$$

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[1] O. W. Richardson, The Electron Theory of Matter, second edition, page 233.

that is,

$$\frac{d\xi}{\xi(1 - G\xi)} = \frac{d\beta}{\beta(1 - \beta^2)},$$

and

$$\int \frac{d\xi}{\xi(1 - G\xi)} + h = \int \frac{d\beta}{\beta(1 - \beta^2)} + k,$$

or

$$\log \left[\frac{1 - G\xi}{\xi}\right] \cdot \left[\frac{\beta}{\sqrt{1 - \beta^2}}\right] = h - k = \text{const.} = \gamma.$$

Therefore,

$$\left[\frac{1 - G\xi}{\xi}\right]\left[\frac{\beta}{\sqrt{1 - \beta_2}}\right] = e^\gamma = \text{const.} = \delta;$$

that is,

$$\xi(G\beta + \delta\sqrt{1 - \beta^2}) = \beta;$$

whence

$$\xi \equiv \lambda(\beta) = \frac{\beta}{G\beta + \delta\sqrt{1 - \beta^2}}. \tag{27}$$

where G and δ are arbitrary constants independent of β.

Whatever G and δ may be, it will always be true that

$$M_L = m_L.$$

It follows, then, that as far as the *longitudinal* mass is concerned, the electron may expand to any extent whatever, and yet, the relation $M_L = m_L$ will always be true. If, however, we are to have the additional equality between M_t and m_t, that is, if we are also to have the relation

$$M_t = m_t$$

true for *all* velocities, then $G \cdot \lambda(\beta)$ must necessarily be equal to 1; that is, *there can be no uniform dilatation of the electron.* It is clear that this does not mean that a uniform expansion may not *actually* take place. What has been proved is that, if we *accept* Lorentz's formulæ for the transverse and longitudinal masses to be the *correct ones*, then *there can be no uniform dilatation* of the electron if the longitudinal and transverse masses given by (22) and (23) respectively are to be identical with those of Lorentz's formulæ for *all velocities.*

I am glad to tender my thanks to Professor G. F. W. Swann for the interest shown in the results herein described.

DEPT. OF PHYSICS,
THE UNIVERSITY OF MINNESOTA,
MINNEAPOLIS,
March 19, 1922.

MAXWELL'S LAW OF DISTRIBUTION OF VELOCITIES AND THE PRINCIPLE OF PROJECTIVE COVARIANCE.

By I. Maizlish.

Synopsis.

Derivation of Maxwell's Law of Distribution of Velocities with the Aid of the Principle of Projective Covariance.—In the ordinary derivation of this law there occurs a functional equation of the form: $g(x_1)g(x_2)g(x_3)g(x_4) = \psi(x_1^2 + x_2^2 + x_3^2 + x_4^2)$, whose solution is usually obtained on the supposition that the functions are differentiable. In this paper the solution is obtained without making use of the assumption, by applying the author's principle of projective covariance.

1. In the derivation of Maxwell's law of the distribution of velocities among a large number of molecules there occurs a certain functional equation whose solution is usually obtained by differentiation. The assumptions on which the solution is based are:

I. The functions occurring in the functional equation are continuous, single-valued, and real;
II. The independent variables are real;
III. The functions are differentiable.

2. Now it is known that a function may be continuous and yet not have a derivative. It is therefore desirable to inquire whether the functional equation can be solved without making use of assumption III. The object of this paper is to indicate a method of doing this by making use of the Principle of Projective Covariance. The problem will be generalized somewhat in that we shall consider it as a problem in a 4-dimensional space (S_4).

3. Consider, then, an S_4 and let x_1, x_2, x_3, x_4 be the rectangular coördinates of a point in this space. If we are dealing with a gas containing a large number (N) of molecules per unit volume, the *position* of any molecule will be known as soon as we know the values of x_1, x_2, x_3, x_4 appropriate to this molecule. Each molecule may therefore be represented by a single point in S_4. The points which are occupied by molecules will be called *molecular-points.* Let us now find the number of molecular-points for which

$$x_i \text{ lies between } x_i \text{ and } x_i + dx_i \quad (i = 1, 2, 3, 4). \qquad (R)$$

4. Let $Ng(x_i)dx_i$ be the number of molecular-points for which x_i lies between x_i and $x_i + dx_i$; $i = 1, 2, 3, 4$. The same function, g, is used

for $i = 1, 2, 3, 4$, on account of the isotropy of S_4. If we now *assume* that x_1, x_2, x_3, x_4 are independent of each other, the number of molecular-points for which x_1, x_2, x_3, x_4 lie within the range (R) is

$$\Delta_4 N dx_1 dx_2 dx_3 dx_4 = Ng(x_1)g(x_2)g(x_3)g(x_4)dx_1 dx_2 dx_3 dx_4; \qquad (1)$$

and, therefore, the number per unit volume is

$$\Delta_4 N = Ng(x_1)g(x_2)g(x_3)g(x_4). \qquad (2)$$

The rectangular axes x_1, x_2, x_3, x_4 are, however, entirely arbitrary. Equation (2) must therefore be a function of the radius vector only; that is, we must have

$$g(x_1)g(x_2)g(x_3)g(x_4) = \psi(x_1^2 + x_2^2 + x_3^2 + x_4^2). \qquad (A)$$

This is the functional equation the solution of which will be obtained without making use of assumption III. We shall restrict our interest solely to the continuous solution of (A).

5. In order to see more clearly how equation (A) follows from the assumptions made, we will prove the following

THEOREM: *A necessary and sufficient condition in order that a function $F(x_1, x_2, x_3, x_4)$ be invariant under any orthogonal transformation is that it be a function of the radius vector only; that is, that*

$$F(x_1, x_2, x_3, x_4) = \psi(x_1^2 + x_2^2 + x_3^2 + x_4^2).$$

It will then follow that a necessary and sufficient condition that

$$g(x_1)g(x_2)g(x_3)g(x_4)$$

be invariant under any such transformation is that it be a function of the radius vector only.

PROOF: (*a*) The condition is sufficient. For let y_1, y_2, y_3, y_4 be the new variables, and

$$\begin{vmatrix} a_{11} & a_{12} & a_{13} & a_{14} \\ a_{21} & a_{22} & a_{23} & a_{24} \\ a_{31} & a_{32} & a_{33} & a_{34} \\ a_{41} & a_{42} & a_{43} & a_{44} \end{vmatrix}$$

the matrix of the transformation. By hypothesis,

$$\begin{aligned} F(x_1, x_2, x_3, x_4) &= \psi(x_1^2 + x_2^2 + x_3^2 + x_4^2), \\ &= \psi(y_1^2 + y_2^2 + y_3^2 + y_4^2), \end{aligned}$$

because an orthogonal transformation is defined as a linear transformation such that

$$x_1^2 + x_2^2 + x_3^2 + x_4^2 \equiv y_1^2 + y_2^2 + y_3^2 + y_4^2.$$

By substitution,

$$\psi(y_1^2 + y_2^2 + y_3^2 + y_4^2) = F(y_1, y_2, y_3, y_4);$$

and

$$F(x_1, x_2, x_3, x_4) \equiv F(y_1, y_2, y_3, y_4).$$

(*b*) The condition is necessary. For we have

$$\begin{aligned} F(x_1, x_2, x_3, x_4) &\equiv F(y_1, y_2, y_3, y_4) \\ &\equiv F\left(\sum_{k=1}^{4} a_{1k}x_k, \sum_{k=1}^{4} a_{2k}x_k, \sum_{k=1}^{4} a_{3k}x_k, \sum_{k=1}^{4} a_{4k}x_k\right). \end{aligned}$$

In the last equation place $x_2 = x_3 = x_4 = 0$. The result is

$$F(x_1, 0, 0, 0) \equiv F(a_{11}x_1, a_{21}x_1, a_{31}x_1, a_{41}x_1).$$

Thus, F must be of such a form as to be independent of a_{11}, a_{21}, a_{31}, and a_{41}. Since, however, a_{11}, a_{21}, a_{31}, and a_{41} cannot all be equal to 1, and, moreover, since the only condition existing between them is

$$a_{11}^2 + a_{21}^2 + a_{31}^2 + a_{41}^2 = 1,$$

we see that this must be the form in which they enter in F. This will in general be the case if and only if

$$F(a_{11}x_1, a_{21}x_1, a_{31}x_1, a_{41}x_1) \equiv \psi[(a_{11}x_1)^2 + (a_{21}x_1)^2 + (a_{31}x_1)^2 + (a_{41}x_1)^2].$$

This is to be true for all values of $a_{11}x_1$, $a_{21}x_1$, $a_{31}x_1$ and $a_{41}x_1$. Hence, if we replace $a_{k1}x_1$ by

$$a_{k1}x_1 + a_{k2}x_2 + a_{k3}x_3 + a_{k4}x_4, \quad k = 1, 2, 3, 4;$$

the result is that

$$\begin{aligned} &F\left(\sum_{k=1}^{4} a_{1k}x_k, \sum_{k=1}^{4} a_{2k}x_k, \sum_{k=1}^{4} a_{3k}x_k, \sum_{k=1}^{4} a_{4k}x_k\right) \\ &\qquad = \psi\left[\left(\sum_{k=1}^{4} a_{1k}x_k\right)^2 + \left(\sum_{k=1}^{4} a_{2k}x_k\right)^2 + \left(\sum_{k=1}^{4} a_{3k}x_k\right)^2 + \left(\sum_{k=1}^{4} a_{4k}x_k\right)^2\right]; \end{aligned}$$

that is,

$$\begin{aligned} F(x_1, x_2, x_3, x_4) &\equiv F(y_1, y_2, y_3, y_4) \\ &= \psi(y_1^2 + y_2^2 + y_3^2 + y_4^2). \end{aligned}$$

But, in virtue of the relations existing between the coefficients of the matrix (M), it follows immediately that

$$\psi(y_1^2 + y_2^2 + y_3^2 + y_4^2) \equiv \psi(x_1^2 + x_2^2 + x_3^2 + x_4^2).$$

Therefore,

$$F(x_1, x_2, x_3, x_4) = \psi(x_1^2 + x_2^2 + x_3^2 + x_4^2).$$

The theorem is therefore proved.

6. The Principle of Projective Covariance[1] enables us to obtain the solution of the functional equation (A) with ease. This Principle asserts that the equations occurring in Physics are covariant under the transformation:

$$\begin{aligned} \xi_1 &= G(\sigma, r)x_1, \\ \xi_2 &= G(\sigma, r)x_2, \\ \xi_3 &= G(\sigma, r)x_3, \\ \xi_4 &= G(\sigma, r)x_4, \end{aligned} \tag{3}$$

where G is an arbitrary function of the distance (r) of any point from the origin of a system of coördinates in S_4, and an arbitrary constant σ; and x_1, x_2, x_3, x_4 are the Minkowski variables. To fix our ideas, consider the following special form of (3):

$$\begin{aligned} \xi_1 &= n^{\sigma-r^2}\,x_1, \\ \xi_2 &= n^{\sigma-r^2}\,x_2, \\ \xi_3 &= n^{\sigma-r^2}\,x_3, \\ \xi_4 &= n^{\sigma-r^2}\,x_4, \end{aligned} \tag{4}$$

where n is any number greater than 1. We have

$$g(x_1)g(x_2)g(x_3)g(x_4) = \psi(x_1^2 + x_2^2 + x_3^2 + x_4^2). \tag{A}$$

By the Principle of Projective Covariance, we also have

$$g(\xi_1)g(\xi_2)g(\xi_3)g(\xi_4) = \psi(\xi_1^2 + \xi_2^2 + \xi_3^2 + \xi_4^2). \tag{B}$$

In equation (A) set $x_2=x_3=x_4 = 0$, and in equation (B) set $\xi_2 = \xi_3 = \xi_4 = 0$. The result is

$$g^3(0)g(x_1) = \psi(x_1^2),$$

and

$$g^3(0)g(\xi_1) = \psi(\xi_1^2).$$

Hence, since, from physical considerations, $g(0)$ exists,

$$\frac{\psi(x_1^2)}{g(x_1)} = \frac{\psi(\xi_1^2)}{g(\xi_1)}. \tag{5}$$

7. Now ξ_1 may be looked upon as an independent variable. For, despite the fact that x_1 and ξ_1 are connected by the transformation (4), the value of ξ_1 is not determined by x_1 alone: it also depends on x_2, x_3, and x_4. But then, the left-hand side of equation (5) is a function of x_1 only, and the right-hand side is a function of ξ_1 only. Hence, equation (5) can only be true if each member of this equation is equal to a constant. Therefore,

$$\frac{\psi(x_1^2)}{g(x_1)} = \text{const.} = \beta^3, \text{ say.} \tag{6}$$

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[1] I. Maizlish, PHYSICAL REV., July, 1921.

8. In equation (*A*) set $x_2 = x_3 = x_4 = 0$. The result is

$$g(x_1)g^3(0) = \psi(x_1^2);$$

from which, by equation (6), we get

$$g^3(0)\frac{\psi(x_1^2)}{\beta^3} = \psi(x_1^2);$$

that is,

$$g(0) = \beta. \tag{7}$$

Moreover, from equation (*A*) it is easily seen that

$$g(0)g(0)g(x_1)g(x_2) = \psi(x_1^2 + x_2^2),$$

that is,

$$\beta^2 g(x_1)g(x_2) = \psi(x_1^2 + x_2^2). \tag{8}$$

Multiply each member of equation (8) by β^4. Thus,

$$\beta^3 g(x_1)\beta^3 g(x_2) = \beta^4\psi(x_1^2 + x_2^2),$$

that is,

$$\psi(x_1^2)\psi(x_2^2) = \beta^4\psi(x_1^2 + x_2^2) \tag{9}$$

by substitution from (6). Now divide each member of (9) by β^8. The result is

$$\frac{\psi(x_1^2)}{\beta^4}\cdot\frac{\psi(x_2^2)}{\beta^4} = \frac{\psi(x_1^2 + x_2^2)}{\beta^4};$$

and, on placing

$$\varphi(x) \equiv \frac{\psi(x)}{\beta^4}, \tag{9^1}$$

this becomes

$$\varphi(x_1^2)\varphi(x_2^2) = \varphi(x_1^2 + x_2^2). \tag{10}$$

The last equation may be written

$$\varphi(x)\varphi(y) = \varphi(x + y), \tag{11}$$

by placing $x = x_1^2$, and $y = x_2^2$.

9. Now the functional equation (11) has been solved by Cauchy,[1] Darboux,[2] and others. Assuming that φ is continuous, single-valued, and real; and that x and y are real, Cauchy has shown that the *only* (continuous) solution of (11) is

$$\varphi(x) = a^x,$$

where a is an arbitrary constant. But these assumptions are identical with those we made at the beginning. Hence, from eqs. (10) and (11) we get

$$\varphi(x_1^2) = a^{x_1^2}.$$

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[1] Cauchy, Œuvres (2), 3 (1897), p. 98.

[2] Darboux, Math. Ann., Bd. 17, 1880, p. 56.

In view of eqs. (6) and (9[1]) we now have

$$a^{x_1^2} = \varphi(x_1^2) = \frac{\psi(x_1^2)}{\beta^4} = \frac{\beta^3 g(x_1)}{\beta^4};$$

$$\therefore \quad g(x_1) = \beta a^{x_1^2}. \tag{12}$$

Thus, in general,

$$g(x_i) = \beta a^{x_i^2}, \quad (i = 1, 2, 3, 4). \tag{13}$$

10. It follows that the number of molecular-points for which x_1, x_2, x_3, x_4 lie within the range (R) is, by (1) and (13),

$$\Delta_4 N dx_1 dx_2 dx_3 dx_4 = N\beta^4 a^{[x_1^2+x_2^2+x_3^2+x_4^2]} dx_1 dx_2 dx_3 dx_4;$$

and the number per unit volume is therefore:

$$\Delta_4 N = N\beta^4 a^{[x_1^2+x_2^2+x_3^2+x_4^2]}. \tag{14}$$

The constant a is arbitrary: we may therefore put it equal to e^{-h}, where e is the Napierean base, h is a constant, and the minus sign is prefixed to the h for otherwise $\Delta_4 N$ would increase indefinitely with $(x_1^2 + x_2^2 + x_3^2 + x_4^2)$. Thus, equation (14) may be written as

$$\Delta_4 N = N\beta^4 e^{-h[x_1^2+x_2^2+x_3^2+x_4^2]}. \tag{15}$$

11. The solution obtained is a generalization of Maxwell's. By putting $x_4 = 0$, and remembering that $g(0) = \beta$, equation (15) reduces to

$$\Delta_3 N = N\beta^3 e^{-h[x_1^2+x_2^2+x_3^2]} \tag{16}$$

12. We may regard x_1, x_2, x_3 as any set of rectangular axes in a space of three dimensions (S_3). Take these axes as the components of a velocity c defined by

$$c^2 = u^2 + v^2 + w^2;$$

where

$$x_1 \equiv u,$$
$$x_2 \equiv v,$$

and

$$x_3 \equiv w.$$

Making this substitution, (16) becomes

$$\Delta_3 N = N\beta^3 e^{-h[u^2+v^2+w^2]}.$$

13. The number of molecules for which u, v, w lie within the range u and $u + du$, v and $v + dv$, w and $w + dw$, respectively, is now seen to be

$$\Delta_3 N dudvdw = N\beta^3 e^{-h[u^2+v^2+w^2]} dudvdw,$$

which is the solution given[1] by Maxwell.

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[1] Maxwell, Collected Papers, Vol. I., p. 381.

14. Thus, provided we justify every step in the process of arriving at equation (A), and restrict our interest to the continuous solution of this equation, under the specified conditions, the solution (solutions) depends (depend) on that (those) of

$$\varphi(x)\varphi(y) = \varphi(x + y). \tag{C}$$

But under the same restrictions as those specified at the beginning of this paper, there is *only one* solution of (C). Hence, there is only *one* solution of (A), and, by the application of the Principle of Projective Covariance, this has been shown to be

$$g(x) = \beta e^{-hx^2}.$$

I am grateful to Professor R. W. Brink, of the Department of Mathematics, for examining the manuscript.

Dept. of Physics,
The University of Minnesota,
Minneapolis,
March 23, 1922.

A MODIFICATION OF VAN DER WAALS' EQUATION.

By W. P. Boynton and Arthur Bramley.

Synopsis.

The proposed equation is $(p + a/v^2)(v - b) = RT/(1 + \psi^2/T^2)$, where ψ is a characteristic temperature. It represents the behavior of CO_2 and other substances more closely and gives better values of the ratio T_c/p_cv_c. While the corrective factor is purely arbitrary, it resembles those of certain theoretical equations having a rational basis and also lends itself to mathematical treatment. It is shown that not only the energy but also the specific heat and entropy derived from this equation approach zero values at absolute zero in agreement with conclusions from the researches of Nernst.

Theoretical formulæ for specific heat (c_v), *internal energy and entropy* as functions of T and v, are derived from thermodynamic laws and the equation of state given above.

I. Introduction.

THE authors have attempted to derive an equation of state which shall be more satistactory than those previously proposed. To be of value such an equation must describe the behavior of actual substances to some degree of approximation, and must be mathematically tractable. If it fails in the first point, it is worthless; if in the second, useless. It is more satisfying if it also has a rational basis.

An excellent example of such an equation is the familiar formulation of the Boyle-Charles laws,

$$pv = RT,$$

which has a rational basis in the kinetic theory of gases, is a very useful first approximation, and is exceedingly tractable. It is confessedly only a first approximation, describing merely the "ideal" (or perfect) gas. A typical second approximation is the famous equation of van der Waals,

$$(p + a/v^2)(v - b) = RT,$$

which also has a rational basis, is quite fairly tractable, and corresponds qualitatively to the behavior of substances capable of existing in both the gaseous and liquid forms, including such phenomena as the critical state, and by the aid of thermodynamical considerations, the coexistence and equilibrium of the two states.

II. Thermodynamic Relations.

A satisfactory equation of state must be consistent with the fundamental laws of thermodynamics, and conversely, the laws of thermodynamics are sufficient to determine the forms of the equations for specific heat, entropy, internal energy and other thermodynamic properties, provided an equation of state is employed which gives a sufficiently close approximation to the facts of the behavior of substances.

The familiar formulation of the first and second laws, on the assumption that the only work is that against external pressure, is

$$TdS = dU + pdv,$$

where

$$S = \text{entropy},$$
$$U = \text{internal energy}.$$

This may be expanded to the form

$$TdS = \frac{\partial U}{\partial T}dT + \left(\frac{\partial U}{\partial v} + p\right)dv.$$

The ordinary transformations lead to the relations

$$\frac{\partial S}{\partial T} = \frac{1}{T}\frac{\partial U}{\partial T}; \quad \frac{\partial S}{\partial v} = \frac{1}{T}\left(\frac{\partial U}{\partial v} + \mathrm{p}\right); \quad \frac{\partial U}{\partial v} = T\frac{\partial p}{\partial T} - p; \quad \frac{\partial S}{\partial v} = \frac{\partial p}{\partial T}.$$

Discarding the usual easy but unnecessary assumption that the specific heat is a constant, independent of temperature, its value may be found as follows. Differentiating partially by T the value of $\partial U/\partial v$,

$$\frac{\partial^2 U}{\partial T \partial v} = \frac{\partial p}{\partial T} + T\frac{\partial^2 p}{\partial T^2} - \frac{\partial p}{\partial T} = T\frac{\partial^2 p}{\partial T^2},$$

and integrating with respect to v,

$$\frac{\partial U}{\partial T} = c_v = T\int \frac{\partial^2 p}{\partial T^2}dv + f(T).$$

The ordinary assumptions that p is a linear function of T and that c_v is a constant evidently constitute a special case of this general relation. From this value of c_v and the relations given above as existing between the various partial derivatives it is possible to deduce values for U and S.

$$U = \int\left[\left(T\int\frac{\partial^2 p}{\partial T^2}dv\right)dT + \left(T\frac{\partial p}{\partial T} - p\right)dv\right] + \int f(T)\,dT,$$

$$S = \int\left[\left(\int\frac{\partial^2 p}{\partial T^2}dv\right)dT + \frac{\partial p}{\partial T}dv\right] + \int\frac{f(T)}{T}dT.$$

III. Proposed Equation of State.

The researches of Nernst at low temperatures have led to the formulation of his "heat theorem" which states that the temperature coefficient of any property of a body, which varies with the temperature and approaches a finite limiting value as the temperature is lowered, is zero. This theorem leads to the conclusion that the specific heat of all substances approaches zero as the temperature is lowered, a result which is verified by experiment.

This theorem has also lead Planck and others to state that the entropy approaches the limiting value zero at the absolute zero.

These two conditions, namely the zero values of c_v and of S, together with the obvious fact that the internal energy, U, must also vanish at the absolute zero of temperature, determine completely the boundary conditions at the lower limit. An inspection of the generalized thermodynamic equations obtained above shows that the condition that S shall vanish at the absolute zero can only be satisfied if p is such a function of T that $\partial^2 p/\partial T^2$ does not vanish identically.

The assumptions of the kinetic theory that the pressure and the internal energy of a gas are both associated with the kinetic energy of the rectilinear motion of its molecules lead to the suggestion that c_v and the gas constant R may be at least similarly related to the temperature. Attempts have been made to find a rational formula for c_v as a function of the temperature. Of these two at least have been fairly successful, that of Debye based upon the quantum hypothesis, and the other, of A. H. Compton[1] based upon the notion of agglomeration of molecules. Curves plotted from these two equations agree fairly closely with each other as well as with the experimental data, but both are transcendental in form and hence do not lend themselves readily to mathematical manipulation. For that reason we are suggesting the use of the algebraic form

$$\frac{k^2T^2}{1+k^2T^2},$$

in which k is the reciprocal of a temperature. Comparing this with Compton's form

$$\frac{C}{C_\infty} = e^{-\tau/T}\left(\frac{\tau}{T}+1\right)$$

for the particular value $k = 5/3\tau$, the resulting curves are in substantial agreement for all values of T/τ above 0.5, within that range differing by amounts varying from 0.001 to 0.007; but below that point the difference is greater, the algebraic form exceeding the other at the most by about 0.06. Nevertheless the simpler algebraic curve is of the same general form, and may be regarded as a permissible approximation to the more exact but also more complicated rational form, when the main purpose is a general qualitative description only. Following this suggestion we assume that

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[1] Physical Review (2), 6, pp. 377–389, 1915.

$$R = R_{\infty}\frac{T^2/\psi^2}{1 + T^2/\psi} = R_{\infty}/(1 + \psi^2/T^2),$$

where ψ is a characteristic temperature, and write a modified form of van der Waals' equation

$$(p + a/v^2)\,(v - b) = R^{\infty}T/(1 + \psi^2/T^2).$$

From this equation the critical data can be derived without difficulty and the ordinary form of the equation in reduced coördinates obtained, except that θ, the "reduced" temperature, will be a somewhat complicated function of T, T_c and ψ. Substituting from this modified equation of state the partial derivatives of p in the thermodynamically derived equations for c_v, U and S, we obtain, dropping the subscript of R,

$$c_v = 2\,R\frac{3\psi^4/T^4 - \psi^2/T^2}{(1 + \psi^2/T^2)^3}\,ln\,(v/b - 1) + f\,(T),$$

$$U = 2\,R\,T\frac{\psi^2/T^2}{(1 + \psi^2/T^2)^2}\,ln\,(v/b - 1) - a/v + a/b + \int_0^T f(T)dT,$$

$$S = R\frac{3\psi^4/T^4 + \psi^2/T^2}{(1 + \psi^2/T^2)^2}\,ln\,(v/b - 1) + \int_0^T \frac{f(T)}{T}\,dT.$$

These functions have been integrated with respect to v between the limits b and v, and since $v = b$ only when $T = O$, the product $T^2 ln(v/b - 1)$ and similar terms involving higher terms of T all vanish at the lower limit.

We shall assume that we may write

$$f(T) = \Sigma M\frac{k^2T^2}{1 + k^2T^2},$$

that is, as one term, or a sum of terms, of the form suggested. Since the mathematical behavior of the sum is similar to that of a single term, we may perform the integrations indicated, and write as a special case

$$f(T) = M\frac{k^2T^2}{1 + k^2T^2},$$

$$\int_0^T f(T)\,dT = M\int_0^T \frac{k^2T^2}{1 + k^2T^2}dT = M\left(T - \frac{1}{k}\tan^{-1}kT\right),$$

$$\int_0^T \frac{f(T)}{T}dT = M\int_0^T \frac{k^2T}{1 + k^2T^2}dt = \frac{M}{2}\,ln\,(1 + k^2T^2),$$

in which k is the reciprocal of a characteristic temperature. All these functions vanish for $T = O$, and hence the functions derived as representing c_v, U and S satisfy completely the boundary conditions at the lower limit.

IV. CONCLUSIONS.

We have proposed a modification of van der Waals' equation of the form

$$(p + a/v^2)(v - b) = RT/(1 + \psi^2/T^2),$$

which exhibits the following advantages:

1. For high temperatures it is practically identical with the familiar van der Waals equation, and like it, when volumes also are large, closely approximates the equation of the ideal gas.

2. Like the equation of van der Waals it exhibits the phenomena of the critical state, giving identical formulæ for the critical volume and pressure, but a more complicated one for the critical temperature.

3. The proposed equation gives numerical results which agree with the external behavior of actual substances apparently as closely as any previously suggested equations; *e.g.*, it fits Andrews' data on carbon dioxide fully as closely as does the equation of Clausius, which was developed expressly for that purpose.

4. A common test is the value of the ratio RT_c/P_cv_c which for van der Waals' equation has the value 8/3, while observed values as quoted range mainly from 3.7 to 5.0. This equation gives

$$\frac{RT_c}{p_cv_c} = \frac{8}{3}(1 + \psi^2/T^2_c),$$

which takes the value 3.71 for $T_c/\psi = 1.6$ or the value 5.0 for $T_c/\psi = 1.068$.

5. The value of the specified heat deduced from it shows the proper behavior at low temperatures, and especially in the neighborhood of the absolute zero. The formula deduced, involving as it does the volume v and the possibility that $f(T)$ may be a series of several terms, can be made to conform quite closely to the observed data, even for a substance like water, over a temperature range including one or both changes of state.

6. The expression for the entropy does not involve an infinite constant of integration, but on the contrary vanishes at zero, and has a finite value for finite volumes and temperatures.

Further consideration of the properties of this equation is reserved for future papers.

UNIVERSITY OF OREGON,
EUGENE, OREGON,
February 20, 1922.

THE EFFECT OF NASCENT HYDROGEN ON HARD STEEL MAGNETS.

By John Coulson.

Synopsis.

Aging Effect of Nascent Hydrogen on the Magnetic Moment of Hardened Steel Magnets.—When magnets, well seasoned by repeated heating and cooling, are exposed to the action of nascent hydrogen by being made cathodes in a sulfuric acid bath, the magnetic moment decreases, reaching in time a permanent value from 5 to 20 per cent. less than the original moment. The aging process is accelerated by raising the temperature of the electrolyte, the total time required being only one hour or less at 60° C. For *drill rod* (carbon 1.2 per cent.), quenched from 800° C., the change occurs gradually; but for *tungsten magnet steel* most of the decrease occurs suddenly after an exposure which, for the electrolyte at 60° C., varies from 3 to 15 minutes as the quenching temperature is increased from 700 to 850° C., the corresponding sudden changes in moment decreasing from 19 to 4 per cent. The behavior of *spring steel* (carbon 0.8 per cent.) is very similar, but the sudden changes occur later. After aging in this way, hammering the magnets has practically no effect.

Penetration of Nascent Hydrogen into Mild Steel.—Photographs of fractured cold-rolled rods show that in 40 seconds the hydrogen penetrated about 1 mm.

The magnetic moment of *permanent* magnets changes quite perceptibly even following the most careful "aging"[1] after magnetization. This so-called aging effect goes on at a diminishing rate notwithstanding such magnets be kept isolated in a neutral field. The desirability of hastening the final condition, where the magnetic moment ceases to change, led to the present investigation.

Bar magnets of "Special Alloy Magnet Steel" and high carbon steels were treated electrolytically in a strongly acidulated electrolyte. It was found that the magnetic moment of magnets treated as cathode undergoes a marked diminution, and that the character of the change depends on the nature of the steel and on the hardening temperature.

Careful and elaborate investigations have shown that steel absorbs hydrogen and other gases, and the effect of such gases on the mechanical properties of the metal has been studied in detail.[2] Most of this work, however, has been carried out on steels which were exposed to the gases at temperatures considerably above normal or room temperature. It is not generally accepted that steel absorbs hydrogen to any extent at normal temperatures, therefore, hydrogen is not considered to play here a vital part at ordinary temperatures in the structural or other changes taking place in the metal. Nevertheless, the author,[1] and others[2] have found that nascent hydrogen penetrates steel surprisingly rapidly at temperatures as low as 20° C.

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[1] Wiedemann, Pogg. Ann., 1852, 1858, 1864. Dufour, Pogg. Ann., 99, 1855; Arch. de Geneve, 1857. Favé, Comptes Rendus, 72, 1876. Gaugain, Comptes Rendus, 72, 1876. Trowbridge, Am. Jour. of Science, 1881. Kohlrausch, Wied. Ann., 1884. Barus and Strouhal, Bulletin of the U. S. Geological Survey, No. 14, 1885. Peirce, Am. Jour. of Science, 1896. Durward, Am. Jour. of Science, 1898. Peirce, Proc. Amer. Acad. Arts and Sciences, 1905.

[2] Bellock, Comptes Rendus, 149, 1909. Richards and Behr, Zeitschr. Phys. Chem., 58,

The permeability of steel for hydrogen at these low temperatures suggested that the permanency of the magnetic moment of hardened steel magnets might well be influenced by the absorption of hydrogen. In the course of the investigation fifty or more bar magnets of length 14.4 cm. were carefully made and tested for changes in the magnetic moment after treatment. Most of the specimens were quenched to glass hardness from 850° C. Some were quenched at a lower temperature, about 700° C. It will be seen that the hardening temperature is of great significance in the changes taking place within the steel when hydrogen is absorbed.

Following the hardening process the specimens were magnetized to saturation inside a solenoid many times their length. After removal from the solenoid care was taken to keep the magnets isolated from all magnetic material until their history had been completed. The usual fall in the magnetic moment of the magnets, due to repeated heating and cooling, was observed. This operation was continued until evidence of further change of magnetic moment had disappeared. The heating operation was carried out with the magnet sealed in an air-tight glass tube immersed in boiling water.

The preliminary aging having been completed, the magnet under test was subjected to the action of nascent hydrogen by making it the cathode in an electrolytic cell, while the lead container served as anode. The electrolyte used was a 25 per cent. solution of H_2SO_4, and the current through the cell was kept at 2 amperes. The magnets were exposed to the action of the hydrogen for increasing time intervals, at the outset, usually 15 or 30 seconds. After each exposure the magnetic moment of the magnet was measured at room temperature.

1907. Hein, Zeitschr. Phys. Chem., 58, 1907. Goutal, Comptes Rendus, 148, 1909. Sieverts and Krumhaar, Berl. Deutsche Chem. Ges., 43, 1910. Rumpf, Akad. Wiss. Wien, Sitz. Ber., 119, 1910. Charpy, Bonnerot, Comptes Rendus, 152, 1911. Stead, Iron and Steel Industry, J., 103, 1921; Engineering, 111, 1921. Thompson and Richardson, Met. and Chem. Eng., 16, 1917. Smith, Am. Electro-Chem. Soc. J., 1918.

[1] Coulson, Am. Electro-Chem. J., 1917.

[2] Bellaty and Lussana, R. Istituto Veneto Atti., 1888; 1891. N. Cimento, 5, 1913. Charpy and Bonnerot, Comptes Rendus, 152, 1911; 154, 1912. Bellaty and Lussana, N. Cimento, 5, Ser. 6, 1913.

The measurements were made by placing on the opposite side of a magnetometer a standard bar magnet in Gauss's A position, held, and protected completely from rapid temperature changes, within a wooden carriage sliding on a horizontal scale. This compensating magnet, having been fixed with its center at a convenient distance d_0 from the center of the magnetometer needle, brought the needle back into the meridian when the center of the magnet under observation was at the fixed distance d. Let M_0 be the magnetic moment of the standard magnet and $2l_0$ its magnetic length, and let M_1 and M_1' be the moments of the magnet under test, before and after treatment respectively, and $2l$ its magnetic length. The needle will be deflected through the angle α so that

$$\frac{2M_0d_0}{(d_0^2 - l_0^2)^2} = \frac{2M_1d}{(d^2 - l^2)^2},$$

$$\frac{2M_1d}{(d^2 - l^2)^2} - \frac{2M_1'd}{(d^2 - l^2)^2} = \frac{2d(M_1 - M_1')}{(d^2 - l^2)^2} = H \tan \alpha,$$

$$\frac{M_1 - M_1'}{M_1} = \frac{(d_0^2 - l_0^2)^2}{2M_0\,d_0} \cdot H \tan \alpha = \frac{\tan \alpha}{\tan \alpha_0},$$

where H is the horizontal component of the earth's magnetic field, and α_0 is the angle through which M_0 would deflect the needle if M_1 were absent.

The method of procedure was then as follows:

The standard magnet was placed with its center at a known distance from the magnetometer, and its carriage clamped firmly in position. The magnet to be tested was placed on the opposite side of the magnetometer and adjusted in such position as to bring the needle back into the meridian. Its holder was then clamped and the distance of the center of the magnet from the magnetometer was recorded. After subjecting the magnet to treatment, it was placed again in its holder and the deflection of the magnetometer needle observed with the magnet at room temperature. The dimensions and the magnetic moment of the standard magnet being known, the magnetic moment and the fractional loss of the moment of the magnet under test could be easily calculated from the above formulæ.

It may be of interest to say that the Special Magnet Steel was a tungsten alloy steel in the form of square bars 8.0 mm. cross section, and was received direct from the Crucible Steel Co., Pittsburgh. The spring steel and polished drill rod were in the form of rods 6.4 mm. in diameter, and were bought in the open market. The carbon content was about 0.80 and 1.20 respectively.

Typical results obtained with magnets of the above materials treated electrolytically at 20° C. and 60° C. are shown, some in tabular form, others by curves. Table I. and Fig. 1 are results obtained for magnets treated at 20° C. The fractional loss of magnetic moment and the corresponding time exposure of the magnet to the action of the hydrogen are given. The upper section of the table and the curve OER of the figure represent observations made on two magnets of drill rod, of which many were tested. For like treatment the results were in very good agreement. Representative data are given in the lower half of the table for a magnet of spring steel, and similar data for a magnet of special magnet steel are shown in curve form, Curve OLV, of the figure.

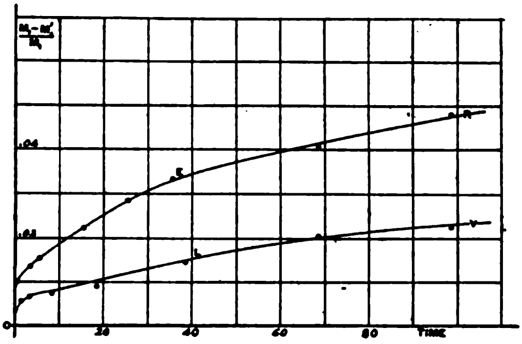

Fig. 1.

Shows the fractional change in the magnetic moment as a function of the time of exposure to the hydrogen at 20° C. Polished drill rod: Curve OER. Special alloy magnet steel: Curve OLV.

TABLE I.

History.	Exposure (Minutes).	$\frac{M_1 - M_1'}{M_1}$.	M.	Exposure (Minutes).	$\frac{M_1 - M_1'}{M_1}$.	M.
Drill Rod.	0		1836	20.0	.0245	1788
Quenched from 800° C.	1.0	.0120	1814	30.0	.0270	1786
Magnetic moment after	3.0	.0150	1809	40.0	.0302	1781
magnetization,	5.0	.0168	1805	50.0	.0320	1777
M = 1836.	10.0	.0198	1800	60.0	.0342	1773
Spring Steel.	0		1919	20.0	.0130	1894
Quenched at 850° C.	0.5	.0030	1913	30.0	.0142	1892
Magnetic moment after	1.5	.0046	1910	40.0	.0158	1889
magnetization,	3.0	.0070	1906	50.0	.0170	1886
M = 1919.	5.0	.0090	1902	60.0	.0175	1885
	10.0	.0111	1898	70.0	.0180	1884

Temperature of exposure: electrolyte kept at 20° C.

Magnets made from drill rod, treated electrolytically, show a greater aging effect than magnets of the other steels. The spring steel magnets change more slowly at the outset than those of special magnet steel, but after 50 minutes' exposure, approximately, the fractional decrease of their respective moments had the same value. Usually after this stage the loss in magnetic moment for magnets of spring steel was greater than for the special magnet steel. From two to three hours' exposure to the electrolytic hydrogen decreased the magnetic moment of the magnet to a fixed value. Hammering the magnets had little or no effect in changing further their magnetic moment. Careful weighing before and after treatment showed that the magnets did not lose weight during exposure.

Numerous magnets of spring steel and special magnet steel, treated at 20° C., showed a sudden drop in magnetic moment before reaching a constant value. It occurred usually after an hour's treatment or more and was of a magnitude of one or two per cent. The change before and after being only a fraction of one per cent.

The rapidity with which the magnetic moment settles to a final value depends on the temperature of the electrolyte in which the magnets are brought under the action of the electrolytically evolved hydrogen. Moreover, the transition to this final state, due to the action of the hydrogen, is surprisingly different for the various specimens.

Table II.

History.	Exposure (Minutes).	$\frac{M_1 - M_1'}{M_1}$.	M.	Exposure (Minutes).	$\frac{M_1 - M_1'}{M_1}$.	M.
Drill Rod.	0		2040	30.0	.101	1834
Quenched from 800° C.	0.5	.0150	2010	40.0	.109	1816
Magnetic moment after	1.0	.0259	1987	50.0	.116	1804
repeated heating and	3.0	.0585	1921	60.0	.121	1793
cooling,	5.0	.0820	1873	80.0	.127	1781
M = 2040.	10.0	.0881	1860	90.0	.129	1777
	20.0	.095	1846			
Special Alloy Magnet	0		1697	10.0	.0129	1675
Steel.	0.5	.0009	1695	20.0	.0538	1650
Original magnet	2.0	.0097	1680	25.0	.0550	1603
moment, M = 1761.	5.0	.0115	1677	35.0	.0565	1601
Moment after repeated						
heating and cooling,						
M = 1697.						
After being dropped 1 ft.						
end on fifty times on a						
block of stone	....	....	....	....	....	..1600

Temperature of exposure: electrolyte kept at 60° C.

Table II. and Fig. 2 show results obtained for magnets of different

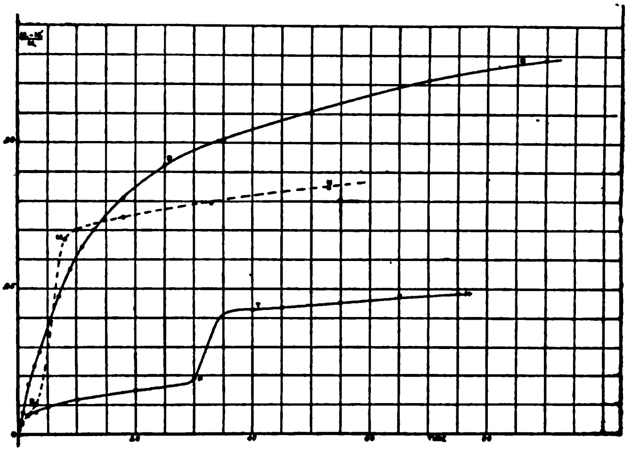

Fig. 2.

Shows the fractional change in the magnetic moment as a function of the time of exposure to the hydrogen at 60° C. Polished drill rod: Curve *ODR*. Special alloy magnet steel: Curve *OMN*. Spring steel: Curve *OPTH*.

material, treated at 60° C. The upper section of the table and the Curve *ODR* of the figure are for magnets made from polished drill rod, quenched at slightly different temperatures to glass hardness. As will be seen, the magnitude of the aging is not the same for the two magnets, but the character of the results is very similar. The final value of the magnetic moment is reached in approximately the same time of exposure. The decrease being about 14 per cent.

The broken Curve *OMN* of the figure and the results tabulated in the lower portion of the table illustrate the character of this aging process on magnets of special alloy magnet steel. The quenching temperature for these magnets differed by about 50° C. The specimen quenched at the lower temperature, 800° C., and indicated by the curve shows a very sudden change in magnetic moment after a few minutes' exposure to the hydrogen in the heated electrolyte. For the specimen quenched at the higher temperature, 850° C., this sudden fall in magnetic moment takes place after a longer exposure. This sudden change in moment is, also, very marked in the case of magnets made of spring steel, but it takes place usually after 20 or 30 minutes' exposure. The curve *OPTH* of the figure is a fair example of results obtained for specimens of this steel when quenched glass hard. Examination of the results will show that after this sudden transition took place the change in the magnetic moment was comparatively small, even after prolonged exposure. Hammering the magnets at this stage caused practically no alteration of the magnetic moment.

This precipitous change in the magnetic moment of magnets made from special magnet steel and from spring steel appears to be considerably magnified when the specimens are quenched at temperatures below 850° C. Table III. shows results obtained with a magnet of special magnet steel quenched at 700° C. These results are shown graphically in Fig. 3, curve *PRTE*. Examination will show that after 2 minutes'

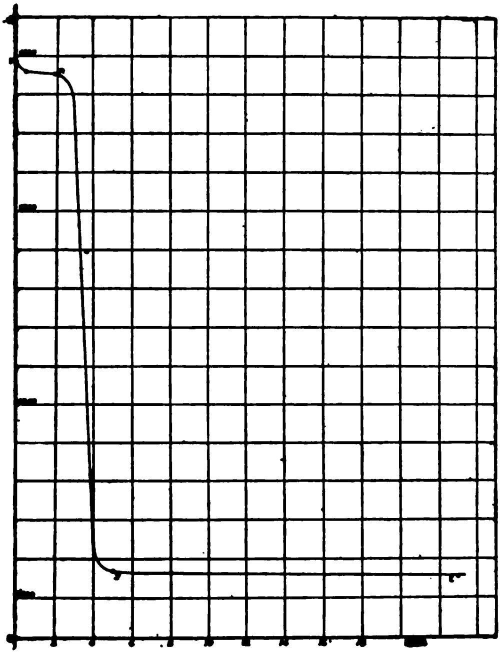

Fig. 3.

Shows the moment of a magnet of special alloy magnet steel quenched at 700° C., as a function of the time of exposure to the hydrogen. Temperature of the electrolyte 60° C.

Table III.

History.	Exposure (Minutes).	$\frac{M_1 - M'}{M_1}$.	*M.*
Quenched from 700° C.	0		1378
Magnetic moment after magnetization,	0.5	.0043	1372
M = 1452.	2.0	.0046	1371
Moment after repeated heating and cooling,	5.0	.1916	1114
M = 1378.	8.0	.1921	1113
	13.0	.1921	1113
	23.0	.1927	1112

Special Alloy Magnet Steel.

Temperature of exposure: electrolyte kept at 60° C.

exposure to the electrolytic hydrogen the magnetic moment of the magnet dropped more than 19 per cent., while up to this point the decrease in magnetic moment was only a small fraction of one per cent. After the sudden change occurred, further exposures to the hydrogen had practically no effect on the magnetic moment.

Fig. 4, which is taken from an earlier paper,[1] illustrates the rapidity with which electrolytic hydrogen penetrates mild steel. *A*, *B*, and *C* are test specimens, 6 mm. in diameter, cut from the same rod of cold-rolled steel. *A* and *B* were broken under stress without exposure to hydrogen. *C*, on the other hand, was broken after an exposure of 40 seconds. The bright band of this test piece indicates the depth of penetration of the hydrogen during this interval.

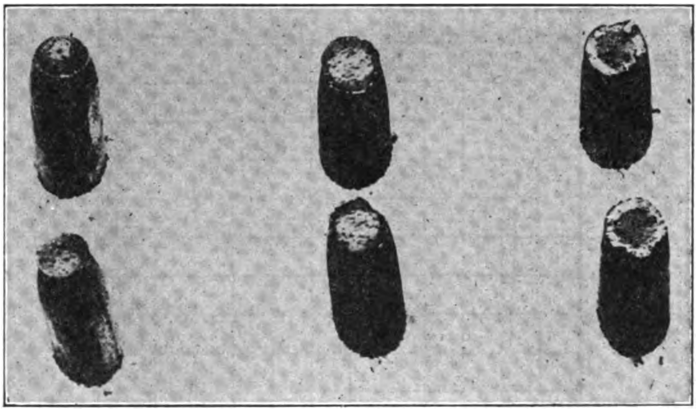

Fig. 4.

Shows the fracture of cold-rolled steel broken under stress. *A* and *B* without exposure to hydrogen. *C* exposed 40 seconds to electrolytic hydrogen. The bright band shows depth of penetration.

An investigation which is in progress on a wide range of steels shows that both the magnetic permeability and the specific resistance decrease on exposure of the metal to the electrolytic hydrogen. It is hoped that when this work is reported, a complete explanation of the changes taking place within the metal will be given.

I wish to acknowledge the valuable assistance given me by Mr. W. O. Smith, who has helped me in all the work.

University of Pittsburgh,
Pittsburgh, Pa.

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[1] Coulson, Am. Electro-Chem. J., 1917.

IMPROVEMENT IN THE DETERMINATION OF THE RADIUM CONTENT OF LOW-GRADE RADIUM-BARIUM SALTS.

By Victor F. Hess and Elizabeth E. Damon.

(Read before the meeting of the American Physical Society, New York, Feb. 25, 1922.)

Synopsis.

Improved Gamma-Ray Method of Determining the Radium Content of Low-grade Radium Salts.—Because of absorption of the rays by the salt, the present gamma-ray method is rather inaccurate for concentrations less than 10^{-6}, and for concentrations above 10^{-7} the emanation method is too sensitive. To bridge the gap, the authors have modified the first method by adopting a shallow container with two curved sides, each concentric with the cylindrical string electrometer used to measure the rays, and only a small fraction of the radius apart. This shape has the effect of making the mean absorption due to the salt small and also very nearly equal to half the maximum absorption. The procedure is to take readings with the container in position (full of the salt to be measured) first alone, then with a small radium tube of known strength placed first just in front and then just in back of the container. The ratio of the first reading to the mean of the other two gives the ratio of the strength of the unknown to the sum of the strengths of the known and unknown within one per cent. The method is both quicker and more accurate than the emanation method for concentrations between 10^{-6} and 10^{-7}. The container used was made of tin plate and was 10 cm. by 10 cm. by 2 cm. thick, the radii being 30 and 32 cm.

Introduction.

The determination of the radium content of highly concentrated radium preparations by means of the gamma-ray method is so well developed that an accuracy of less than one per cent. can be reached in any laboratory where a standardized radium preparation is available. The degree of accuracy becomes less and less when products of lower concentration are to be measured: this is due to the absorption of the gamma rays in the salt itself and also to the fact that the dimensions of these preparations usually are not so small that the differences in distance of the various points of the preparation from the center of the ionization vessel can be neglected. The ordinary gamma-ray methods give sufficient accuracy for salts of 100 per cent. to 1 per cent. radium content (concentration 1 to 10^{-2} g. Ra/g.). If the absorption coefficient of the gamma rays within the salt is known approximately and the absolute amount of salt taken does not exceed about 10 g., sufficient accuracy may be also obtained with salts of 10^{-3} or 10^{-4} g. of radium per gram of salt. For these cases it suffices to assume that the absorption of gamma rays of radium distributed uniformly throughout the substance is equal to the absorption in a layer of half of the actual thickness of the preparation and so make a correction accordingly. But it is not possible to apply the gamma-ray method to salts of very much lower concentration than 10^{-4} g./g. using the customary apparatus: with quantities of 10 g. of salt or less the absolute amount of Radium present is too little to be measured accurately and taking much more salt increases the influence of the absorption within the salt too much. For salts with less than 10^{-4} g. Ra/g. therefore it has been necessary so far to use the emanation method. This method is much less accurate than the gamma-ray method and involves the necessity of dissolving or fusing the salt. With salts of medium concentration (10^{-5} to 10^{-7} g. Ra/g.) it is furthermore necessary to dilute and this brings in a new source of error, not to speak of inconvenience and difficulties of the emanation method in general (difficulties in obtaining saturation current, inconstancy of radium standard solutions, etc.).

Thus it is quite obvious that any extension of the range of the gamma-ray method would be advantageous. The influence of the absorption of gamma rays in the salt itself was computed by E. Schweidler[1] and H. Thirring[2] for the case where the salts are filled into spherical containers of moderate sizes. The correctness of the results depends upon how accurately in any individual case the coefficient of absorption is known. This naturally varies with the size of the crystals and with the method of filling the container. It certainly would not increase the convenience and accuracy of the gamma-ray method when in any case the coefficient of absorption had to be determined by separate experiment.

We found it possible to extend the range of the gamma-ray method for low-grade salts by taking shallow layers of salt within containers of relatively large areas placed in such a way that all points of the surface of the container are at the same distance from the gamma-ray instrument.

PRINCIPLE OF THE METHOD.

This was accomplished by the following arrangement (Fig. 1). The container was a curved tin plate box 10 cm. high and 2 cm. deep. The radius of curvature was 30 cm. and according to this the container was placed at a distance of 30 cm. from the center of the ionization chamber of the electrometer. This was of cylindrical shape so that the surface of the container formed a part of a concentric cylinder plane. The instrument is a string electrometer (electric capacity 1 cm.) devised by one of the authors in 1913 for gamma-ray measurements.

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[1] E. Schweidler, Physik. Zeitschr., Vol. 13, p. 453.

[2] H. Thirring, Physik. Zeitschr., Vol. 13, p. 266, 1912.

It can be foreseen that with such an arrangement the gamma-radiation of a homogeneous radium-barium salt filling the total space between the two cylindric surfaces of the container cannot be very different from the average of the gamma-ray action obtained with the same absolute amount of radium in form of a little standard tube fixed on the outside of the container, front and back (points *B* and *C*, Fig. 1). It is easy to prove this by calculation:

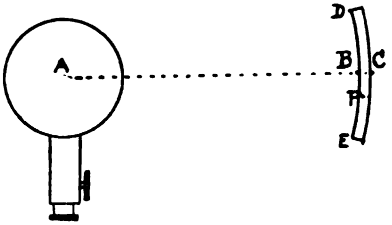

Fig. 1.

We take *P* as an optional point between the two cylindric planes of the container and call $AP = r$, $AB = a$, $AC = a + d$; d represents the thickness of the active layer within the container. We consider the action of the gamma rays of the salt between BC upon the center A of the ionization vessel. The front surface of the container (DBE) is called s. Since d is small compared with the distance AB the volume of the container is $s \cdot d$ and the total amount of radium within the container

$$m = \rho \cdot s \cdot d,$$

where ρ denotes the amount of radium per unit of volume. We call furthermore the coefficient of absorption of the gamma rays of RaC within the radium-barium salt μ and the coefficient of absorption in the material of the wall (zinc) μ'.

Taking a shallow elementary layer (enclosed between two concentric cylinder planes at the distance r and $r + dr$) we obtain the ionization caused by this layer as

$$dI = \frac{K \cdot \rho \cdot s \cdot dr \cdot e^{-\mu(r-a)-\mu' d'}}{r^2},$$

where K denotes the number of pairs of ions caused per ccm. and per sec. by 1 g. of radium (gamma radiation only) at 1 cm. distance (the so-called "Eves number"). $e^{-\mu' \cdot d'}$ denotes the absorption in the zinc plate which forms the front plane of the container (actual thickness $d' = 0.35$ mm.). Since r varies but between a and $a + d$ and we have the square of r in the denominator we may take the mean value $(a + d/2)$ instead of r

as an approximation. The total radiation of the container is then given by the integral

$$I = \frac{K \cdot m \cdot e^{\mu a - \mu' d'}}{(a + d/2)^2 \cdot d} \cdot \int_a^{a+d} e^{-\mu r} \cdot dr$$

and the solution is

$$I = \frac{K \cdot m \cdot e^{-\mu' \cdot d'} \cdot (1 - e^{-\mu \cdot d})}{\mu \cdot (a + d/2)^2 \cdot d} .$$

The same amount of radium *m* concentrated in form of a small tube fixed at *B* (Fig. 1, front of container) would give a gamma-ray action of

$$\frac{K \cdot m}{a^2}$$

and the same tube fixed at *C* (rearside of container)

$$\frac{K \cdot m}{(a + d)^2} \cdot e^{-\mu d - 2\mu' d'},$$

because in this case the gamma rays have to traverse a thickness *d* of salt and twice the thickness of the zinc plate.

The average of these two ionizations is

$$I' = \frac{m \cdot K}{2} \cdot \left[\frac{1}{a^2} + \frac{e^{-\mu d - 2\mu' d'}}{(a + d)^2} \right] .$$

In order to compare *I* and *I′* it is not necessary to know the specific ionization *K* caused by the gamma rays of one gram of radium in our apparatus. Taking the same quantity of radium in both cases and forming the quotient *I*/*I′* we would expect that this quantity is equal to unity if the principle of our method holds.

Substituting numerical values according to the conditions of our experimental arrangement: $a = 30$ cm., $d = 2$ cm., $d' = 0.035$ cm., $\mu = 0.05$ cm.$^{-1}$, $\mu' = 0.35$ cm.$^{-1}$ we obtain

$$\frac{I}{I'} = 0.9914.$$

In other words: considering the action of radium distributed homogeneously in our curved container upon the center of the ionization vessel we would expect 1 per cent. less ionization as the average of ionization corresponding to two readings with the same quantity of radium filled into a small tube fixed first to the front and then to the rear plane of the container.

EXPERIMENTS.

The container was filled with an inactive barium salt and a very small radium tube, containing 0.87 mg. radium element imbedded in the salt at different positions throughout and the ionization measured. The average of these readings was 0.2025 scale divisions/sec. Then the radium tube was taken out and fixed at the center of the front and rear side of the container: there we obtained the readings[1] 0.2232 and 0.1858 ScD/sec. The mean of these two readings, 0.2045, agrees within one per cent. with the average of all readings within the salt, given above. The agreement with the calculation is perfect.

PROCEDURE OF MEASUREMENTS WITH THIS METHOD AND RESULTS AS COMPARED WITH OTHER METHODS.

The procedure of actual determinations of radium content of samples by our method will be best illustrated by an example:

The container was filled with 350 grams of a low-grade radium barium carbonate the radium content of which was unknown, and then hermetically sealed. The first reading was taken not before 3 hours after sealing in order to be sure that the short-lived products RaA–RaC are in equilibrium with the emanation.

All measurements were taken at the same distance (30 cm.) from the center of the gamma-ray instrument.

First simply the gamma-ray action of this filled container was measured and we call this ionization i_1. Then the standard tube (0.87 mg.) was placed in addition to that at the center of the front and afterwards at the center of the rear side of our container. We call the ionization observed in these two cases i' and i'' and take their average

$$i_2 = \tfrac{1}{2}\cdot(i' + i'').$$

The current i_1 corresponds to the action of the unknown quantity of radium x within the container, the current i_2 to x plus the standard. Thus we obtain x, expressed in milligrams from the equation

$$\frac{x + 0.87}{x} = \frac{i_2}{i_1}.$$

Dividing the result x by the known total weight of the radium-barium salt in the container we obtain the radium content of the sample in mg. Ra per kilogram of salt. If the salt is not in radioactive equilibrium the same procedure is repeated several days later and from the known law of recovery of emanation in radium salts the end value computed in the usual way.

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[1] In fact these figures are average figures of at least 5 readings.

In our special example we obtained by this method the result: Radium content of our sample

1.10 mg. per kilogram of salt.

Now this result was checked by two other methods: In the first place a weighed sample of the salt was dissolved in hydrochloric acid, diluted to a proper concentration and then tested by the emanation method. We obtained a result of

1.05 mg. radium per kilogram of salt.

Another weighed sample of our carbonate was dissolved in concentrated sulfuric acid and again tested by the emanation method. With this sample we obtained

1.11 mg. Ra per kilogram of salt.

The agreement of our method with these other methods is as good as can be expected from the possible limits of error of the emanation methods.

Our method has some advantage over the emanation methods: it takes much less time (just two gamma-ray determinations on two different days are necessary) and no decomposition or dilution of the sample is required.

Our method may be used for all materials the Radium content of which lies between 10^{-5} and 10^{-7} g. Ra per gram of material. It fills the gap between the ordinary range of the gamma-ray method and of the emanation method. For materials with less than 10^{-7} g. Ra/g. the emanation method is convenient because it is then no more necessary to dilute the dissolved sample. A remarkable feature of our method is that knowledge of the coefficient of absorption in the salt used is not required.

RESEARCH LABORATORY,
U. S. RADIUM CORPORATION,
ORANGE, N. J.

THE VARIATION OF THE PHOTOELECTRIC CURRENT WITH THICKNESS OF METAL.

By Otto Stuhlman, Jr.

Synopsis.

Silver and platinum deposited in the form of transparent and semitransparent wedges were examined for variation of the photoelectric current as thickness of the metal was increased. The metal was deposited on quartz by the evaporation method and examined when monochromatic light fell on the metal side of the plate.

The results are found to be consistent with the view that the probability of an electron going a given distance without losing its ability to escape falls off exponentially with the distance, when this distance is less than about 40 $\mu\mu$. Up to this thickness there is a parallelism between optical absorption and photoelectric emission. For large wave-lengths this parallelism is more pronounced than for short wave-lengths. For greater wave-lengths optical absorption may increase, but photoelectric emission decreases terminating at the threshold value of photoelectric sensitivity.

The results seem to support the view that photoelectric emission is probably not caused by the absorption of energy from the incident light beam, the light only acting as the agent which sets the electron free from its parent atom.

To test any theory of the photoelectric effect it is necessary to know how the photoelectric current varies with the thickness of the metal through which the electrons must pass and the depth to which the light energy penetrates in the metal. To obtain an adequate conception of the laws governing the penetration of both light and electrons it was thought of primary importance to investigate the change in photoelectric current as the metallic film was increased in thickness.

It was hoped, furthermore, that the results of such an investigation might afford a check on the simple assumption that the number of photoelectrons which escape falls off exponentially with the distance moved in reaching the surface of the metal.

The investigation of the behavior of photoelectrons in passing through metals is confined to a few articles[1–7] which in general agree amongst themselves only in the order of the magnitude of the constants involved. The literature[8] presenting the optical point of view is, however, extensive

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[1] "Density Law of Absorption," Lenard, Ann. d. Phys., 12, p. 730, 1903.

[2] Ladenburg, Ann. d. Phys., 12, p. 558, 1903.

[3] Crother, Phil. Mag., 12, p. 379, 1906.

[4] Rubens u. Ladenburg, Ber. d. D. Phys. Ges., 24, p. 749, 1907.

[5] Partzsh u. Hallwachs, Ann. d. Phys., 41, p. 247, 1913.

[6] Stuhlman, Phys. Rev., 13, p. 132, 1919.

[7] K. T. Compton and Ross, Phys. Rev., 13, p. 374, 1919.

[8] For a summary see Partzsh and Hallwachs, Ann. d. Phys., 41, p. 250, 1913.

though often very contradictory. Whether the light penetrates the metal to a depth of several wave-lengths or only a fraction of a wave-length is still an open question.

Method.—The results were obtained with the apparatus outlined in the writer's above-cited paper[6] and are a continuation of this work and an effort to extend and correlate similar problems investigated by K. T. Compton, Ross, Robinson, Partzsh and Hallwachs and by the writer.

The metals, platinum and silver, were deposited by the evaporation method[1] in the form of wedges, transparent at their thin ends and opaque, or nearly so, at their thick ends. These semitransparent wedges deposited in quartz were then examined for their photoelectric effect at successive millimeter intervals along their lengths, when light from a 110-volt Cooper-Hewitt quartz mercury vapor lamp was allowed to fall at normal incidence on the metal side. A quartz lens of about 20 cm. focal length was used with a slit, which appeared as an image one millimeter in width, when focussed on the metallic wedge under examination. When monochromatic light was used, a Hilger quartz monochromatic illuminator was interposed.

Results.—The curve *ABC* in Fig. 1 shows the characteristic photoelectric emission obtained from a metal as a function of the thickness of the metal, when exposed to the full radiation from the quartz mercury vapor lamp, at normal incidence. Somewhat similar results, though only qualitatively interpretable, were previously published by J. Robinson,[2] and the writer working with K. T. Compton.[3] One possible theoretical treatment of the problem was worked out by Partzsh and Hallwachs.[5] They suggested that if I_p is the intensity of the light which enters and penetrates the surface of the metal, then at a depth x this intensity drops to $I = I_p e^{-\alpha x}$, where α is the coefficient of absorption of the light. From any thickness dx located some distance x below the surface of the metal $nIdx$ electrons start. These are absorbed exponentially in passing back through the thickness x with coefficient of absorption β. The total number emerging is

$$N = nI_p \frac{1 - e^{-d(\alpha+\beta)}}{\alpha + \beta},$$

where d is the thickness of the metal under examination. Three tacit assumptions are involved, namely that the number of electrons which retain their ability to escape falls off exponentially with the distance moved *normally* to the surface, and that the coefficients of absorption of the light and of the electrons are independent of the thickness of the metal.

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[1] Stuhlman, Jour. Optical Soc., 1, p. 78, 1917; PHYS. REV., 13, p. 112, 1919.

[2] Robinson, Phil. Mag., 25, p. 115, 1913; ibid., 32, p. 421, 1916.

[3] Stuhlman and Compton, PHYS. REV. (2), II., p. 208, 1913.

This simple theory leads one to expect the photoelectric current to increase exponentially from zero thickness, to a saturation value comparable to the current obtained from a thick sheet of metal under the usual circumstances. The thickness at which this occurs is then the maximum depth to which the light penetrates the metal.

The extensive curve shown in Fig. 1 was not obtained from a single metallic wedge. At first a wedge very rapidly increasing in thickness was examined. This information gave the general outline of the curve. Then a very thin wedge was examined. This gave the data for the points lying at the beginning of the curve. These detailed data usually covered about the first third of the graph as shown in Fig. 1. Then this wedge was replaced in the deposition apparatus and more metal was deposited, thus increasing the thickness uniformly over the whole surface. Upon examination this second wedge usually furnished the data for the second third of the graph. This was repeated until the saturation value of the photoelectric current curve was obtained. A check on the shape and location of the sink in the curve was obtained by placing two quartz plates end to end and depositing a metal wedge on both simultaneously. In this way the deposit on one plate gave the data for one part of the curve and the deposit on the other the data for the adjoining part.

The thickness of the metal at some point along the wedge was obtained as follows: A quartz plate was covered with a uniform deposit of the metal and matched in color with a similar point on the wedge, to identify its relative position. The photoelectric current from this plate, when exposed under the same conditions as the wedge, was compared with the photoelectric current from the wedge. The thickness of the uniformly deposited plate was determined by weighing, and this thickness identified the thickness of the metallic wedge which produced the same photoelectric current as the uniformly deposited plate.

Where no points of observation are shown on the graphs, it is understood that a combination of several of the above methods furnished the data. Where extrapolations or interpolations are resorted to, the curves are shown by broken lines.

The dotted line in Fig. 1 shows the results to be expected from the above theory on the assumption that the two coefficients are of the same order of magnitude and independent of the thickness of the metal. The experimental data do, in general, conform to this theory especially for large wave-lengths. For the data presented above, however, there exists a marked departure from the simple theory. While the experimental results usually fit the theory for very small and large thicknesses of metal, for intermediate thicknesses there is a marked departure as at *ABC*. Here the curve is seen to pass through a pronounced minimum, *B*, before reaching its saturation value.

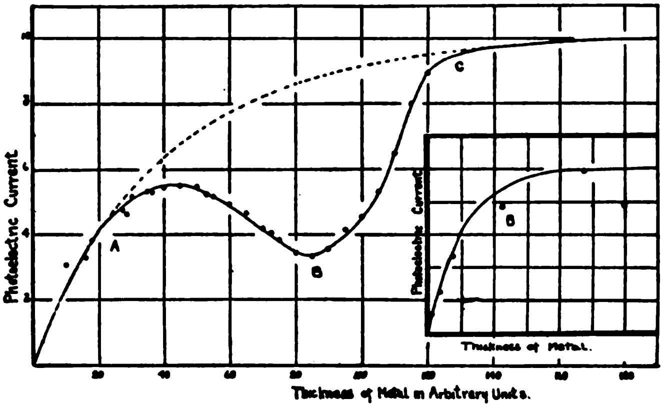

Fig. 1.

The earlier work by the writer and K. T. Compton[11] and J. Robinson[10] also showed an unusual change in the photoelectric current for metallic thicknesses comparable to 10^{-7} cm., apparently out of all proportion to the amount of light absorbed by the metal. Robinson's data stops just short of the point *B* in Fig. 1, hence he interpreted his results as showing an abnormal emission of current for thicknesses comparable to the point *A*. That is, his results are interpreted as showing a maximum in the curve at *A* while the above curve and subsequent data show that the photoelectric current proceeds normally as far as the point *A* and then departs from the theoretically expected current by an apparent subnormal development between *A* and *C*. Beyond *A* the photoelectric current seems to be no longer proportional to the thickness of the metal penetrated by the incident light energy.

In support of this interpretation are quoted some results from an earlier paper by the writer and K. T. Compton[11] shown as an insert in Fig. 1. This curve represents the photoelectric current emitted by a platinum film, cathodically deposited in successively thicker layers on a platinum plate. As in the above curve the current rises exponentially from zero thickness to its maximum, or saturation, value with a small but appreciable variation at the point *B*. This point of observation, at that time attributed to experimental error, lies below the exponential curve drawn through the other points. Here, as before, we meet with a subnormal current, not an abnormal rise in current, for thickness of metal comparable to 10^{-7} cm. Hence with the completed curve before us we must conclude that the photoelectric current is proportional to the thickness of the metal for all values of thickness except such critical values as give an apparent subnormal current.

Results With Monochromatic Illumination.—The work was next extended to determine the change in the photoelectric current with change in frequency of the incident light. Some characteristic results as obtained from silver are shown in Fig. 2. The upper curve shows the photoelectric current from silver as a function of metallic thickness when unresolved light from the quartz mercury vapor lamp fell on the metallic side of the wedge at normal incidence. It shows the approximate average location of the subnormal part of the curve referred to as B in Fig. 1. A cover-glass one millimeter thick was next introduced into the path of the incident beam. Previous examination with a Hilger monochromatic illuminator had shown that this plate absorbed all wave-lengths below λ 3131. The results thus obtained are given by the lower curve of Fig. 2. A Hilger monochromatic illuminator was next introduced into the incident beam and set for λ 2536. These results are shown by the middle curve.

Increasing the wave-length of the incident light-energy shifts the subnormal part of the curve to regions of greater thicknesses.

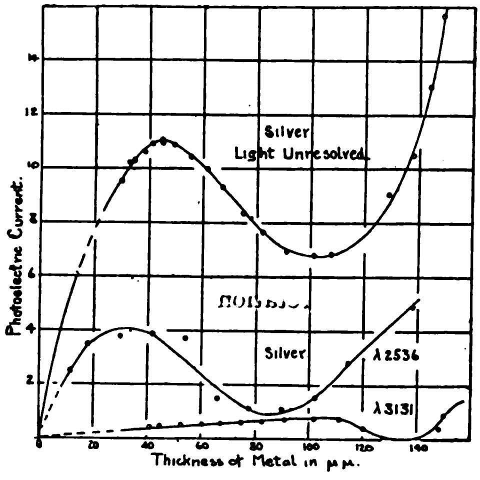

Fig. 2.

A similar comparison with platinum as given in Fig. 3 shows the same effect only to a less degree. If we compare platinum with silver, for wave-length λ 253.6 for wedges deposited under identical conditions, we find that the subnormal position of the curve for silver lies at thickness 90 μμ while platinum has its minimum at about 45 μμ thickness.

Results Due to Fatigue.—It was thought that the slight shift in the minimum of the curve as the wave-length of the incident light-energy decreased was due to aging because of occlusion of gases. Shrinkage in thickness due to aging might account for it, but this possibility was eliminated when the thickness of the metal was determined immediately after the photoelectric current measurements. To test for any change caused by aging due to absorption of gases, a silver wedge was examined directly after deposition (curve No. 1, Fig. 4), then twenty-four hours

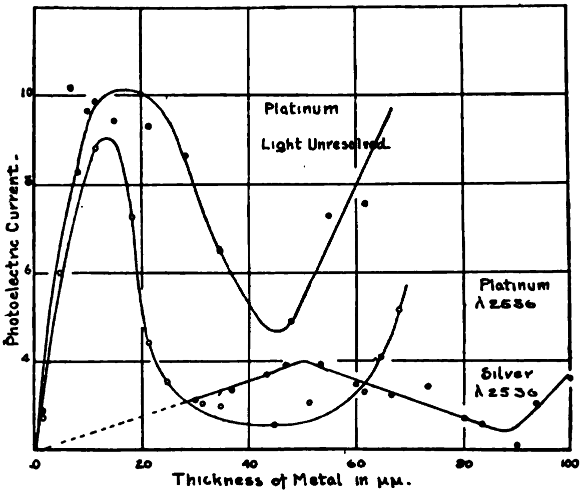

Fig. 3.

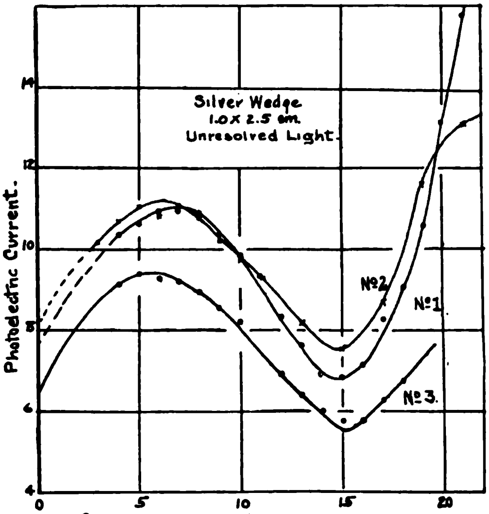

Fig. 4.

later. These latter results are shown by curve No. 2. Then the metal was examined eight days later with the results shown in curve No. 3. These curves show no measurable shift in the location of the minimum, although there is an indication of a slight shift in the position of the peak of the curve, towards the thin end of the wedge. The relative changes in magnitude of the current follow the usual course of changes which accompany "photoelectric fatigue." On the other hand a more detailed examination, of this possible change, with platinum and wave-length 253 μμ, with a nine-day idle period between tests, showed a slight shift of the peak in the curve towards the region of greater thickness. No measurable change in the position of the minimum point, except that which could be accounted for by experimental error, was detected.

We might conclude therefore that for any given metal there is a real departure from the simple saturation curve showing that the thickness of the metal and photoelectric effect are proportional and that this departure appears as an apparent subnormal photoelectric current. The subnormal part of the curve or point of minimum photoelectric emission in the curve shifts to regions of greater thickness as the wave-length of the exciting light increases.

Discussion.—All the curves at the origin have one thing in common, they are either linear or possess a slight curvature concave downward. Robinson's results[10] show his curves as possessing a point of inflexion near the origin, as if the photoelectric current increased at first slowly and then more rapidly with thickness of metal. Theoretically the photoelectric emission and thickness are proportional, as there is a proportionality between absorption of light and thickness of metal.[7, 2]

If the amount of light absorbed is proportional to the resulting photoelectric current then this proportionality is only true for the first 10 μμ thickness of the metal penetrated by the light in case of very short waves, but may reach a thickness of 300 μμ or more for wave-lengths comparable to λ 3130. This initial depth in which exponential absorption takes place, as manifested by the emission of photoelectrons, increases as the wave-length of the incident light-energy increases. It cannot however increase as rapidly as the wave-length increases due to the decrease in kinetic energy of emission of the electrons as the wave-length approaches its photoelectric threshold value.

If the coefficient of absorption for silver as determined by Fritze[1] and later by W. Planck[2] are examined, for wave-lengths lying between 400 and 500 μμ, we find in general an exponential increase in these

[1] Fritze, Ann. d. Phys., 47, p. 763, 1915.

[2] W. Planck, Phys. Zeit., p. 563, 1914.

coefficients with increase in thickness of the metal through which the light penetrates. Their results show a depression in the coefficient of absorption-thickness curve in the vicinity of 50 $\mu\mu$ thickness for λ 546 and what appears to be a shift in this depression to smaller thicknesses as the wave-length decreases to λ 526.

If we examine the absorbing power of these two metals or their transparency, with increasing thickness, we at once notice several interesting analogies. Silver and platinum as examined by Hagen and Rubens for their relative transmission, for a given wave-length as a function of the thickness of the metal, found that a silver surface 80 $\mu\mu$ thick became more and more transparent as the wave-length of the incident energy decreased from λ 7000 to λ 3210. At the latter wave-length the silver transmitted 32 per cent. of the incident energy. From this wave-length down to λ 2210 the surface rapidly became less transparent, reaching a minimum of 1.5 per cent. for wave-length 2210.

Upon comparing equal thicknesses of metal, say 80 $\mu\mu$, we find as shown in Fig. 2, that with decreasing wave-length, the photoelectric results show an increase in the transmission of light by silver. This transmission reaches a maximum at λ 3210. Here the absorption is a minimum but not quite zero. Photoelectrically the light absorption ceases at λ 3250, the threshold value for silver. Beyond this wave-length photoelectric action does not set in again although optical absorption increases very rapidly. If absorption of light and emission of photoelectrons go hand in hand, why does not the photoelectric effect follow the increase in optical absorption? It seems as if the two phenomena at this point were only remotely related or have nothing in common. It appears probable that there are really two phenomena superimposed; the optical absorption which removes energy from the light-wave, and the photoelectric effect which removes no energy from the light-wave. The light appears to act only as the agent reaching into the atom to release a particular electron.

Hagen and Rubens' optical results showed that silver possesses marked regions of selective transmission; a given thickness becoming more and more transparent as the light decreased in wave-length from λ 3160 to λ 2510. This is also verified by the above photoelectric measurements. Where the photoelectric current passes through a minimum the metal must allow most of the incident energy to pass through it without producing a photoelectric effect, so that the light transmitted by this layer is the same as the amount transmitted by a much thinner layer of metal. Under these circumstances it would be impossible to use the transmitted energy as a measure of film thickness as has been done by Compton and Ross.[7]

If we compare the results from silver with those from platinum, say for wave-length λ 2536, we at once notice that the photoelectric current for platinum is very much larger than that for silver, when equal thicknesses of metal are compared. This is also in agreement with the optical absorption of these metals. Hagen and Rubens[1] found that for λ 3210 silver was about one thousand times more transparent than platinum when equal thicknesses of metal (80 $\mu\mu$) were compared. Judging from the photoelectric results and using the assumption that the photoelectric current is proportional to the amount of light absorbed, this magnitude seems very much too large. At most the photoelectric results show platinum only ten times more absorbing than silver. This variation might be accounted for by the great difference in the absorption of the electrons as they pass through the metals. Unfortunately the coefficient of absorption of the electron for platinum is not more than twice as large as that for silver.[2] Again we are confronted with the same difficulty, in that the optical absorption does not allow us to arrive at a conclusion as to the magnitude of the photoelectric current that may be liberated by a metal.

Finally an examination of the photoelectric current for a change in the intensity of the light showed a corresponding change in the magnitude of the current but no measurable shift in the curve along the thickness axis.

Conclusions.

The amount of light absorbed by a metal and the photoelectric current generated as the result of the penetration of the light into the metal are not in general proportional to each other.

If the light penetrating a metal is absorbed according to the known simple exponential law then the photoelectric current is only proportional to the amount absorbed in a depth of metal comparable to less than one tenth a wave-length of the incident energy.

The greater the wave-length of the energy producing photoelectric activity the greater the depth to which absorption of light and emission of current are proportional.

In the case of silver the variation in optical transmission runs parallel to the variation in the photoelectric current as the thickness of metal changes.

Optical absorption of the light may take place without photoelectric emission.

Photoelectric emission is not caused by the absorption of the light energy, but the light acts only as an agent in setting the electrons free from their parent atoms.

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[1] "Durchlässigkeit" as used by Hagen and Rubens, Ann. d. Phys., 8, p. 449, 1902.

[2] Stuhlman, Phys. Rev., 15, p. 549, 1920.

The number of photoelectrons retaining ability to escape falls off exponentially with the distance moved in reaching the surface of the metal. The data presented could not however be used to distinguish between this conclusion and one in which the ability to escape falls off exponentially with the distance moved normally to the surface.

THE UNIVERSITY OF NORTH CAROLINA,
CHAPEL HILL.

NOTE ON THE RATIO OF MASS TO WEIGHT FOR BISMUTH AND ALUMINUM.

By H. A. Wilson.

Synopsis.

The ratio of mass to weight has been shown to be the same for bismuth and aluminum to within one in one million, by the method of Eötvös.

MR. BRUSH[1] has recently described some experiments on the gravitational attractions exerted by several substances and on the ratio of mass to weight for some of them. Contrary to the results of previous experimenters he finds this ratio different for different substances and the attractions per unit mass also different. Mr. Brush's experiments appear to have been conducted with some care and it is not easy to suggest sources of error which might account for his surprising results. In the case of his pendulum experiments he does not state that he corrected for the buoyancy of the air and this effect, if not allowed for, would be sufficient to produce an error of the same order as the differences he found.

Mr. Brush found the greatest difference in the attractions in the case of aluminum and bismuth, so I have made a comparison of the ratios of mass to weight for these two substances by the very excellent method of Eötvös.[2] The result shows that this ratio is the same for these two substances to within one part in one million.

Two small cylinders, one of bismuth and one of aluminum, and each weighing about one gram were attached to the ends of a horizontal aluminum wire six cms. long which was soldered to a vertical wire at its middle point. The vertical wire was suspended by a fine platinum wire, thus forming a torsion balance. A mirror was carried by the vertical wire and the balance was suspended in a suitable metal case having a glass window. The case could be turned about a vertical axis on a stand provided with levelling screws. A telescope, provided with illuminated cross wires in its eye-piece was attached to the case and the apparatus could be adjusted so that the image of the cross wires formed by light reflected from the mirror could be made to coincide with another cross wire in the eye-piece.

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[1] Phys. Rev. (2), XIX., p. 125, 1921.

[2] Mathematische und Naturwissenschaftliche Berichte aus Ungarn, Bd. 8, S. 64, 1891.

The case was turned so that the balance beam was approximately East and West and was then turned through two rightangles. It was found that after turning through two rightangles the image of the cross wires came to rest not more than one quarter of a millimeter from its previous position in the eye-piece. The lower end of the vertical wire of the balance dipped into a small vessel containing castor oil which gave sufficient damping. To prevent twisting of the torsion wire when the case was turned through two rightangles stops were provided which carried the beam round with the case. These stops were put in position after the telescope was adjusted so that the image coincided with the cross wires and were removed after the case had been rotated.

The time of one complete vibration of the beam was about three minutes.

The theory of the experiment is as follows. Owing to the rotation of the earth part of the attraction of the earth on a body is used up in keeping the body on its circular path.

If r denotes the radius of the earth and ω its angular velocity, then in latitude θ, the horizontal component of the centrifugal force on a body of mass m is $mr\omega^2 \cos\theta \sin\theta$. The attraction of the earth is mg towards its center so that if ϕ denotes the inclination of the apparent weight to the earth's radius

$$\phi = \frac{r\omega^2 \cos\theta \sin\theta}{g}.$$

For another body suppose

$$\phi' = \frac{r\omega^2 \cos\theta \sin\theta}{g'}.$$

If the two bodies have nearly equal masses and are suspended East and West on a torsion balance, as in Eötvös' experiment, there will be a couple acting on the balance equal to $mgd\,(\phi - \phi')$ where d is half the length of the balance.

If T is the time of one oscillation of the balance $T = 2\pi d\sqrt{2m/\mu}$, where μ is the torsion coefficient of the wire. Hence $\mu = 8\pi^2 md^2/T^2$. The couple $mgd\,(\phi' - \phi)$ will twist the wire through an angle Δ given by

$$\mu\Delta = mg\,(\phi' - \phi)\,d.$$

When the apparatus is turned through two rightangles the wire will be twisted through an angle 2Δ and

$$2\Delta = \frac{2mg\,(\phi - \phi')\,d}{\mu} = \frac{(g - g')\,T^2 r\omega^2 \cos\theta \sin\theta}{4\pi^2 g'}.$$

If t denotes the time of one revolution of the earth then $\omega = 2\pi/t$ and

$$\frac{g - g'}{g'} = (2\Delta)\ \frac{2dt^2}{rT^2 \sin 2\theta}.$$

For Houston $\theta = 30°$ so with $T = 180$ secs. $g = 980$ and $d = 3$ cms. we get

$$\frac{g - g'}{g'} = 25 \times 10^{-4} \times (2\Delta).$$

The experiments showed that 2Δ was less than about 1/2500, so that $(g - g')/g'$ was less than about 10^{-6}.

We conclude therefore that the acceleration of gravity is the same for bismuth and aluminum to within one part in one million.

Rice Institute,
Houston, Texas,
March 25, 1922.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

MINUTES OF THE WASHINGTON MEETING, APRIL 21 AND 22, 1922.

THE 115th regular meeting of the American Physical Society was held at the Bureau of Standards in Washington, D. C., on Friday and Saturday, April 21 and 22, 1922. There were morning and afternoon sessions on both days, with an attendance of about one hundred and seventy-five members and visitors. The presiding officers were Theodore Lyman and Charles E. Mendenhall, President and Vice-President of the Society, respectively. The Association of Apparatus Manufacturers held sessions upon the same days. On the evening of Friday, April 21, there was a joint dinner, held in the dining room of the Bureau of Standards, at which there were addresses by Director S. W. Stratton, Professor R. A. Millikan and Professor F. K. Richtmyer. There was also a very interesting exhibit of scientific apparatus.

There was a meeting of the Council on the afternoon of Friday, April 21, 1922, attended by fourteen members. There were important discussions regarding the report of the Educational Committee and with regard to the development of the PHYSICAL REVIEW. One candidate was elected to Fellowship and thirty-two were elected to membership, as follows: *Elected to Fellowship*; Otto Maass: *Elected to Membership*; Norman I. Adams, Donald S. Ainslie, George W. Alderman, O. S. Duffendack, David C. Duncan, Scott B. Ewing, O. Rex Ford, George S. Gessner, George E. Gibson, Helen G. Rafsky, A. L. Greenlees, William W. Harper, Kalman Heindlhofer, August Hund, G. E. M. Jauncey, Robert V. Kleinschmidt, Raymond G. Lehnhoff, James B. Macelwane, W. C. McQuarrie, Duncan MacRae, George R. Miller, Leslie F. Murch, Brian O'Brien, W. H. Pielemeier, Samuel Robinson, Allen G. Shenstone, James J. Smith, Robert B. Sosman, M. N. States, Alma T. Waldie, Usaburo Yoshida, J. F. T. Young, W. C. Geer, Walter S. Huxford, Edwin L. Rose.

The following program of sixty-two papers was presented; seven of these, Nos. 28, 29, 33, 42, 43, 56 and 60 were read by title:

1. Characteristic X-Ray Absorption in the "L" Series for Elements N62 to N77. J. M. CORK.

2. Effect of Temperature on the X-Rays Scattered by Crystals. G. E. M. JAUNCEY.

3. The Effect of Occluded Hydrogen upon the Crystalline Space-Lattice of Palladium. L. W. McKeehan.

4. X-Ray Limits Beyond the Range of Spectroscopic Measurements. F. L. Mohler and Paul D. Foote.

5. Precision Measurements of the Alkali Halides. Wheeler P. Davey.

6. Total Reflection of X-Rays from Glass and Silver. Arthur H. Compton.

7. The Crystal Structure of Strontium Selenide. Mabel K. Slattery. Introduced by Edna Carter.

8. A New Method of Using X-Rays in Crystal Analysis. William Duane and George L. Clark.

9. A Study of Secondary Valence by Means of X-Rays. George L. Clark and William Duane.

10. The Scattering of X-Rays at Small Angles. A. R. Duane and William Duane.

11. Note on the Size of the Electron as Determined by the Absorption and Scattering of X-Rays. F. K. Richtmyer.

12. Short Electric Waves. E. F. Nichols and J. D. Tear.

13. The Optical Constants of Certain Liquids for Short Electric Waves. J. D. Tear.

14. A Mechanical Model for Hysteresis. A. Press.

15. The Variation of the Photoelectric Current with Thickness of Metal. ✓✓ Otto Stuhlman, Jr.

16. Free Modes of Oscillation in Loop Aerials. S. L. Brown and C. P. Boner.

17. Improved Experiments on Magnetization by Rotation. S. J. Barnett and L. J. H. Barnett.

18. The Effect of a Longitudinal Magnetic Field on the Mechanical Properties of a Vibrating Nickel Wire. C. V. Kent and B. J. Babbitt. Introduced by H. M. Randall.

19. Theory of End-Loss Corrections and Their Application to Tungsten Filaments in Vacuo. A. G. Worthing.

20. Effect of the Current Distortion by Long Lines on the Operation of Recording Relays. Carl Kinsley.

21. The Calculation of the Capacity of Antennas. Frederick W. Grover.

22. Direct Capacity Measurement. George A. Campbell.

23. The Complete Scale of Color Temperature and its Application to the Color Grading of Daylight and Artificial Illuminants. Irwin G. Priest.

24. A Simple and Accurate Method for Determining Surface Tension and Density of Molten Glass. Edward W. Washburn.

25. New Proof of the Specular Reflection of Molecules. R. A. Millikan and Karl S. Van Dyke.

26. Radial Flow in Rotating Liquids. Harold Mottsmith and Irving Langmuir.

27. Noises in Stressed Metals. Barry MacNutt and A. Concilio.

28. The Simple Rigidity of Drawn Tungsten Wire at Incandescent Temperatures. William Schriever.

29. The Reversible Inductivity of Rochelle Salt under High Frequency Fields. John G. Frayne.

30. Reciprocal Diffraction Relations Between Circular and Elliptical Plates. John Coulson and G. G. Becknell.

31. A Flow Calorimeter for Measuring the Heat Capacity of Gases. H. F. Stimson, T. S. Sligh and N. S. Osborne.

32. Elastic Constants of Solid Rods at High Frequencies. W. G. Cady.

33. The Influence of the Surface Tension on the Efflux of a Liquid in Jet-Form. Julius Hartmann. Introduced by Hugo Fricke.

34. A Study of the Luminous Discharge in Hydrogen and in Mercury and a New Method of Measuring Ionization Potentials. George E. Gibson and W. Albert Noyes, Jr.

35. Excitation of the Spectra of Hydrogen and of Nitrogen in Low-Voltage Arcs. O. S. Duffendack. Introduced by K. T. Compton.

36. The Relative Intensities of Stark Effect Components in the Helium Spectrum. John Stuart Foster.

37. Cathodoluminescence of Heated Alumina. D. T. Wilber.

38. Radiation from Oxides. I. Emissive Power in Red of Zirconium Oxide. W. E. Forsythe.

39. Variation of Contact Difference of Potential with Temperature in Potassium and Sodium, and the Accompanying Changes in Photo-Electric Emission. Herbert E. Ives.

40. A Precision Rotating Sector: Aperture Variable and Measurable While in Motion. A. H. Pfund.

41. Specific Intensity of Radiation in an Absorbing Medium. Leigh Page.

42. Phenomena in Gases Excited by Radio Frequency Currents. E. O. Hulburt.

43. On the Effect of Short Electromagnetic Waves on a Beam of Electrons. C. J. Lapp.

44. Effect of the Initial Emission Velocities of Electrons on the Minimum Arcing Voltage in Gases. K. T. Compton and Y. T. Yao.

45. The Independence of the Arcing Voltage in Mercury Vapor on the Nearness of the Liquid Surface. Y. T. Yao.

46. Mobilities of Electrons in Hydrogen. Leonard B. Loeb.

47. The Electron Emission from Thoriated Tungsten Filaments. Irving Langmuir.

48. The Removal of Thorium from the Surface of a Thoriated Tungsten Filament by Bombardment with Positive Ions. K. H. Kingdon and Irving Langmuir.

49. The Measurement of Magnetic Field Strength by Means of Electron Tubes. Albert W. Hull.

50. A General Relation for Electron Emission from Metals. Saul Dushman.

51. The Secondary Electron Emission from Nickel. C. Davisson and C. H. Kunsman.

52. An Experimental Method of Testing the Expressions for Longitudinal and Transverse Masses of the Electron. L. T. Jones and W. C. Pomeroy.

53. Oil Drop Experiments as Proof of the Invariance of Electric Charge. F. W. Loomis.

54. Study of the Hydrogen Radiation in the Red and the Infra-Red. F. S. Brackett.

55. The Voltage-Current Relation in Central Anode Photo-Electric Cells. Herbert E. Ives and Thornton C. Fry. ✓✓

56. The Broadening of the Balmer Lines of Hydrogen with Pressure. E. O. Hulburt. ✓✓

57. Crystal Structures of Vanadium, Germanium and Graphite. Albert W. Hull.

58. The Diffusion Coefficient in Solids and Its Temperature Coefficient. Saul Dushman and Irving Langmuir.

59. Note on the Cohn-Minkowski Formula for the Motion of an Insulator in a Magnetic Field. S. J. Barnett.

60. A New Method for the Generation of Sound Waves. Julius Hartmann. Introduced by Hugo Fricke.

61. The Effect of a Magnetic Field on the Absorption of X-Rays. Joseph A. Becker. Introduced by F. K. Richtmyer.

62. Formation and Life of Metastable Helium. Fabian M. Kannenstine.

The abstracts of papers in the above program, with corresponding numbers, are given on the following pages.

Dayton C. Miller,
Secretary.

1. CHARACTERISTIC X-RAY ABSORPTION IN THE "L" SERIES FOR ELEMENTS N62 TO N77.

By J. M. Cork.

Using photographic method and the Tungsten emission lines as standard, the wave-length of the three L bands was determined.

The square root of frequency plotted with atomic[1] numbers (combined with measurements of other observers), give lines with curvature upward for increasing atomic number.

Combination of the absorption frequencies with that of the emission lines[2] help to determine the energy levels in such modifications of the Bohr-Sommerfeld atom as proposed by Wentzel and Smekal.

With such energy levels established a uniform notation for emission lines which would tell their origin, is suggested.

University of Michigan.

[1] Hertz, Z. für P., 3, p. 19. Duane, P. N. A. S., 6, p 509. DeBroglie, C. R., 170, p. 585.

[2] Hjalmar, Z. für P., 7, p. 341.

2. EFFECT OF TEMPERATURE ON THE X-RAYS SCATTERED BY CRYSTALS.

BY G. E. M. JAUNCEY.

ACCORDING to Debye (Ann. der Phys., Band 43, 1914, pp. 47–95) the intensity of the x-rays scattered by a crystal at a given angle is proportional to $1 - e^{-M}$, where M is a function of the ratio of the temperature of the crystal to the characteristic temperature.

Applying Debye's formulæ to calcite, for which A. H. Compton gives the characteristic temperature as 910° K., and assuming 20 as the average atomic weight of the atoms of the calcite molecule, the ratio of the intensity of the scattered radiation at 70° with the primary rays when the temperature of the crystal was 565° K. to that when the temperature was 290° K. was calculated on the assumption of (1) no zero-point energy (2) zero-point energy. Assuming a wave-length of .30 Å.U. the values of the ratio are (1) 2.22 and (2) 1.32.

A calcite crystal was heated to the above temperatures and the ratio observed was 1.05 with certainly an error no more than 15 per cent. The effective wave-length of the rays was about .30 Å.U. It would appear that Debye's theory is incorrect. This experimental result is supported to some extent by a theoretical paper by L. Brilloun (Ann. de Phys., Jan.–Feb., 1922, p. 88) in which he throws some doubt on the theory of Debye.

WASHINGTON UNIVERSITY,
ST. LOUIS, MO.,
April 6, 1922.

3. THE EFFECT OF OCCLUDED HYDROGEN UPON THE CRYSTALLINE SPACE-LATTICE OF PALLADIUM.

BY L. W. MCKEEHAN.

THE crystalline space-lattice of palladium is face-centered cubic, and the edge of the unit cube is about 3.90×10^{-8} cm. Hydrogen is readily absorbed by thoroughly annealed metal at room temperature and atmospheric pressure, and increases the parameters of the space-lattice by as much as several per cent., without altering its type. There is evidence, however, that the space-lattice is locally distorted by the introduction of the hydrogen atoms. Whether these take the places of palladium atoms or occupy intermediate positions cannot as yet be determined because of the great differences in weight and scattering power between atoms of the two elements.

RESEARCH LABORATORIES,
WESTERN ELECTRIC COMPANY.

4. X-RAY LIMITS BEYOND THE RANGE OF SPECTROSCOPIC MEASUREMENTS.

BY F. L. MOHLER AND PAUL D. FOOTE.

DIFFERENCES in absorption limits adequately explain all x-ray emission lines of heavy elements. The authors have extended computations of limits to light elements thus supplementing data obtained from critical potential measurements below the range of x-ray spectroscopy. It has been shown before that the K series starts with the ionization potential of helium and the limits L_1 and L_2 from neon. For light elements we found other L limits softer than L_1 and these too give by combination K emission lines. Kurth's measurements of radiation from solids instead of gases indicated single L limits for aluminum and silicon much higher than L_1. These two points fall on the extrapolated L_3 line. We suggest the hypothesis that radiation from outer L orbits is suppressed in solids just as arc radiation is. For this reason the emission spectra observed by Millikan may belong to the L_3 series. Extrapolation of the M series shows that the ionization point of argon and the softest x-ray limits of potassium and nickel as measured by the authors, and of iron and copper (as measured by Kurth) belong to the series M_1M_2. Three higher potentials measured by Kurth fall close to M_5.

BUREAU OF STANDARDS,
April 5, 1922.

5. PRECISION MEASUREMENTS OF THE ALKALI HALIDES.

BY WHEELER P. DAVEY.

USING the method described at the February meeting for making precision measurements of the x-ray diffraction patterns of crystals, the dimensions of the halides of Cs, Rb, K and Na have been determined with an accuracy of 0.1 per cent. The data presented will be published shortly in full in the PHYSICAL REVIEW. The data show two interesting features. (1) The difference in "distance of nearest approach" of centers of $\overset{+}{\mathrm{Cs}}$ and $\overset{+}{\mathrm{Rb}}$ in the iodide, bromide, and chloride is constant to within experimental error. The same statement may be made of $\overset{+}{\mathrm{Cs}}$ and $\overset{+}{\mathrm{K}}$, but not of $\overset{+}{\mathrm{Cs}}$ and $\overset{+}{\mathrm{Na}}$. The difference in "distance of nearest approach" of centers of $\overset{-}{\mathrm{I}}$ and $\overset{-}{\mathrm{Br}}$ in the Cs, Rb and K salts of these halogens is constant to within experimental error. The same statement may be made of $\overset{-}{\mathrm{I}}$ and $\overset{-}{\mathrm{Cl}}$. (2) Since, in the case of the Cs compounds, the "distance of nearest approach" is measured along the cube-diagonal of the crystal, and in the case of the Rb and K compounds it is measured along the cube-edge of the crystal, it appears from the constant values obtained for (CsI–CsBr), (RbI–RbBr) and (KI–KBr) that $\overset{-}{\mathrm{I}}$ and $\overset{-}{\mathrm{Br}}$ act as though they were spherical in shape. A similar statement can be made of $\overset{-}{\mathrm{Cl}}$.

RESEARCH LABORATORY,
GENERAL ELECTRIC CO.,
SCHENECTADY, N. Y.

6. TOTAL REFLECTION OF X-RAYS FROM GLASS AND SILVER.

BY ARTHUR P. COMPTON.

IF the frequency of the radiation traversing a medium is considerably greater than the natural frequency of vibration of any of the component electrons, the index of refraction of the medium should be $n = 1 - Ne^2/2\pi mf^2$. Here N is the number of electrons per unit volume, e and m have their usual values, and f is the frequency of the radiation. Since this index is less than unity, such radiation should be totally reflected from a polished surface if the angle of incidence is greater than the critical angle.

Experiments have been performed which show that regular reflection of x-rays does occur at angles of a few minutes of arc from polished surfaces of glass and silver, and that except near the critical angle the greater part of the incident energy is reflected. The critical angles for the reflection of $\lambda = 1.279$ Å.U. from plate glass and silver mirrors have been measured, giving values of $1 - n = 5.0 \times 10^{-6}$ and 20.9×10^{-6} respectively. Taking the number of electrons per atom to be the atomic number, the corresponding theoretical values are 5.2 and 19.8×10^{-6}. The agreement is thus quite satisfactory.

WASHINGTON UNIVERSITY,
SAINT LOUIS,
April 5, 1922.

7. THE CRYSTAL STRUCTURE OF STRONTIUM SELENIDE.

BY MABEL K. SLATTERY. INTRODUCED BY EDNA CARTER.

SRSE was prepared by heating the selenate to a red heat in a stream of hydrogen. Its x-ray diffraction pattern was photographed according to the powder method. The thirteen lines obtained fit a simple cubic lattice with $d = 3.10$ Å. Density measurements show the unit structure to be a cube of dimensions 3.10 Å., the alternate corners being occupied by Sr and Se ions. This structure is similar to that of KCl and RbBr.

VASSAR COLLEGE,
POUGHKEEPSIE, N. Y.

8. A NEW METHOD OF USING X-RAYS IN CRYSTAL ANALYSIS.

BY WILLIAM DUANE AND GEORGE L. CLARK.

IN this method either a small crystal (a volume of .25 cubic mm. suffices) or crystal powder may be employed.

In analyzing a small crystal we place it on the axis of rotation of an x-ray spectrometer, fix the ionization chamber at some convenient angle, 2θ, from the zero line of the instrument and send through it a beam of rays belonging to the continuous x-ray spectrum (not the line spectra). We then turn the crystal through a series of small angles and measure the ionization current at each step. When any one of the crystal's principal planes makes the angle θ

with the incident beam it picks out the x-rays of wave-length λ, given by the equation

$$n\lambda = 2d \sin \theta \qquad (1)$$

and reflects them into the ionization chamber, producing a marked increase in the current. The curves shown represent the ionization current as a function of the angular position of the crystal in an experiment with a potassium iodide crystal. The angular distances between the sharply marked peaks on the curves are the angles between the respective reflecting planes in the crystal.

To get the distance between successive planes in any one set we place the crystal so that this set of planes reflects the x-rays into the ionization chamber and then reduce the voltage applied to the tube. When the voltage reaches the value, V, given by the equation

$$Ve = h\nu = \frac{hc}{\lambda},$$

it no longer can produce x-rays of length λ, and, for the first order spectrum, $n = 1$, practically vanishes. The point at which the current vanishes appears to be sharply marked. The values of V and θ substituted in equations (1) and (2) give the required distance, d. The only other quantity that enters into the computations is the universal constant $hc/e = 12{,}354$, if V is in volts and λ in Ångströms.

Our experiments with the potassium iodide crystal indicate a simple cubic structure (in agreement with Davey and Wyckoff), the length of the cube's edge being 3.532×10^{-8} cm. Assuming one atom of each element to a cube this gives for the density 3.111, in close agreement with the value measured by Baxter, 3.114.

If the crystal is in the form of powder, we place it at the center of the spectrometer, fix the ionization chamber at some angle, 2θ, as above, and measure the ionization current with different voltages applied to the tube. The curve representing the ionization current as a function of the voltage has breaks in it at voltages corresponding to the vanishing of the x-rays reflected by the different sets of crystal planes. Equations (1) and (2) give the distance between successive planes in each set.

HARVARD UNIVERSITY.

9. A STUDY OF SECONDARY VALENCE BY MEANS OF X-RAYS.

BY GEORGE L. CLARK AND WILLIAM DUANE.

THE ability of electrically neutral molecules to combine with other molecules capable of existing free, such as inorganic salts with water to form hydrates, with ammonia to form ammines and with molecular halogens to form polyhalides, is attributed to secondary valence forces residing in the stray fields of atoms and ions. The uncertainty and confusion in this subject has led to the present researches. Numerous remarkable relationships between the stabilities of secondary valence complexes and the dimensions of the atoms and molecules comprising them have been established and will be published in a separate paper. The only possible method of correlation of these relationships and of discovering how the complexes are formed and constituted is analysis by means of x-rays. The first compound studied in this way was potassium tri-iodide, $KI.I_2$. The crystal preserved against sensible decomposition by very special precautions was analyzed by the x-ray method described in the previous paper. It was found to be centered cubic, with an iodine *atom* going to the center of each of the original unit cubes of KI and thereby expanding them from an edge length of 3.532 to 4.680×10^{-8} cm. Experimentally $n = \rho d^3/\text{Mol. Wt.} \times \text{Wt. H atom}$, where n is the number of molecules per unit cube, and ρ the density, was found to be .4986 or ½. At an angle of 6° 45′ the ionization current vanished at a voltage of 11,400. The structure accounts for a great many of the properties of $KI.I_2$. Studies are now in progress on $CsI.I_2$ where CsI itself is centered cubic with a value of d of 4.562×10^{-8} cm., upon other polyhalides and upon some ammines and hydrates beginning with those of the lithium halides.

HARVARD UNIVERSITY.

10. THE SCATTERING OF X-RAYS AT SMALL ANGLES.

BY A. R. DUANE AND WILLIAM DUANE.

MANY of the experiments performed in this laboratory during the last eight years on the short wave-length limit of the continuous x-ray spectrum show that the ionization current in the ionization chamber of an x-ray spectrometer becomes exceedingly small, when the angle made by the chamber with the direct beam of rays has been reduced to a value less than that at which the crystal can reflect the rays. The experiments with crystal powders described in the papers presented at this meeting by G. L. Clark and one of us show the same effect. All of these results indicate that the amount of radiation scattered by the reflecting substance at angles less than that of reflection becomes very minute in comparison with the reflected radiation.

The object of the research described in this paper has been to test various substances for this phenomenon. We fix the material to be examined at the center of an x-ray spectrometer, and measure the ionization current with the chamber in different positions. The curves in the slide shown give the currents as functions of the angles in an experiment with a sheet of aluminium. The currents represent the secondary and scattered radiation from the aluminium. The curves indicate that this radiation reaches a well-defined maximum at an angle of about 13° from the direction of the primary beam of rays, and that, as this angle decreases, the radiation also decreases, reaching a very small value at a sharply marked angle of 9°.7. Making corrections for the natural leak of the instrument and for stray radiation we find that the radiation from the aluminium at angles smaller than 9°.7 can not amount to as much as one per cent. of that at the maximum.

On the assumption that the radiation at angles greater than 9°.7 is largely due to reflection from the planes containing the aluminium atoms we can calculate the maximum distance between these planes. The equation

$$Ve = \frac{hc}{\lambda}$$

gives us the minimum wave-length, λ, in the x-ray beam, and the equation

$$\lambda = 2d \sin \theta$$

gives us the distance, d, between the planes. A correction for the widths of the slits, amounting to 0°.8, has to be added to 9°.7 in order to get the true angle. Substituting half of the angle 9°.7 + 0°.8 and the value of the voltage, V, used in the experiment, namely 29,350 volts, in the equations, we get $d = 2.32$ Ångströms. The greatest distance between the planes in aluminium given by A. W. Hull is 2.33, in close agreement with our value.

It appears from this research that the scattering from such a substance as aluminium may be treated as largely due to reflection from planes. Many other substances have been examined with similar results,[1] for instance water and wood.

Harvard University.

11. Note on the Size of the Electron as Determined by the Absorption and Scattering of X-Rays.

By F. K. Richtmyer.

J. J. Thompson's expression for the absorption and scattering of x-rays

$$\frac{\mu}{\rho} = KN^4\lambda^3 + \frac{\sigma}{\rho}$$

has been verified by the writer and others down to $\lambda = .09$ Å. Extrapolation for aluminum to $\lambda = 0$ gives a value of $\sigma/\rho = .15$, some 25 per cent. smaller than the theoretical value $(8\pi/3)(e^4/m^2)n = .20$ as derived by Thompson. Whereas the value of μ/ρ for gamma rays is known to be of the order of .05. Accordingly A. H. Compton modifies the above expression to

$$\frac{\mu}{\rho} = \phi_f N^4\lambda^3 + \phi_s \frac{\sigma_0}{\rho}$$

where ϕ_f and ϕ_s are coefficients whose value depends on the ratio of the wave-length of the x-rays to the diameter of the (ring) electron, which Compton computes to be 1.85×10^{-10} cm.

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[1] During the progress of our research a paper by Hewlett appeared in the March number of the Phys. Rev., p. 267, in which he mentions having observed a reduction of the radiation scattered from carbon at small angles. Further, an interesting report on scattering of x-rays has been sent to us by Professor A. H. Compton, in which he suggests an explanation of Hewlett's observation similar to that we proposed for our results. Professor Compton's report will be published shortly by the National Research Council.

Data on aluminum, previously reported by the writer, and more recently by Duane, give values of the mass absorption coefficient which are 7.5, 25, 50, and 90 per cent. higher than Compton's computed values at wave-lengths, respectively, of .20, .15, .125, and .10 Å., although Compton's formula and the writer's data agree for $\lambda > .30$ Å. This indicates an electron much smaller than computed by Compton.

Taking the scattering coefficient, as determined by extrapolation of data over the region $.20 < \lambda < .40$ Å., at .15, and using Compton's formula, an electron of diameter 1×10^{-11} cm. gives a scattering coefficient of .057 at $\lambda = .005$ Å.

CORNELL UNIVERSITY.

12. SHORT ELECTRIC WAVES.

BY E. F. NICHOLS AND J. D. TEAR.

METHODS for the generation and isolation of radiation of a few millimeters' wave-length have been developed. The generator finally adopted is based upon the principle of the Hertzen oscillator. It embodies a number of new features making possible the generation of very short waves.

The receiver is the Nichols radiometer. Receiving elements of either 1 μ platinum wire of proper length for resonance with the incident radiation, or of platinum films deposited by distillation upon thin mica are substituted for the usual blackened radiometer vanes. By proper choice and adjustment of vanes, the receiver may be made either selective or non-selective.

For securing greater homogeneity, a reflecting echelon made of carefully machined brass blocks spaced at intervals of $\lambda/2$ was used and found to reflect selectively. Two such reflecting echelons with steps at right angles when placed one after the other in the path of the beam give, under suitable conditions, a fair approximation to monochromatic radiation. Mountings for these echelons have been designed easy of adjustment to any desired spacing. Even one such echelon can be made to give an approximate analysis of the incident radiation.

At present the shortest wave-length isolated is 1.8 mm. The shortest observed, but not reproducible at will, is 0.8 mm.

NELA RESEARCH LABORATORIES,
CLEVELAND, OHIO,
March 29, 1922.

13. THE OPTICAL CONSTANTS OF CERTAIN LIQUIDS FOR SHORT ELECTRIC WAVES.

BY J. D. TEAR.

THE coefficients of reflection and absorption of water, glycerin, methyl and ethyl alcohol for the wave-lengths 4, 8, and 18 mm. have been measured, and the refractive indices computed by the Cauchy-Quincke formula.

A second measure of the refractive index has been obtained in a few cases by measuring the reflection from a thin layer of the liquid over a mercury surface.

As the thickness of the layer is varied, the reflected energy passes through maxima and minima giving a measure of the wave-length in the liquid.

The results as obtained by the two methods agree within the limits of experimental error.

NELA RESEARCH LABORATORIES,
CLEVELAND, OHIO,
March 29, 1922.

14. A MECHANICAL MODEL FOR HYSTERESIS.

By A. PRESS.

THE model comprises a slider spring constrained with respect to a frame. The slider is frictionally mounted, adjustably upon the frame runway. Mounted on the slider is a movable yoke, spring constrained with respect to the slider. The motion of the yoke with respect to the frame registers the magnetic displacement B with respect to the force H impressed on the yoke. The stored energy in the slider spring corresponds to the energy of I and the energy in the yoke spring that due to H (for a vacuum). The frictional constraint of the slider corresponds to the hysteresis loss factor and is proportional to I and not H. Various types of loops are obtained by making the frictional coefficient a function of the slider displacement by means of wedge-shaped surfaces. Magnetic saturation is simulated by affecting the displacement factor for the slider springs. The model furnishes a complete analog of mechanical and electrical as well as magnetic hysteresis.

WASHINGTON, D. C.

15. THE VARIATION OF THE PHOTOELECTRIC CURRENT WITH THICKNESS OF METAL.

By OTTO STUHLMAN, JR.

SILVER and platinum deposited in the form of transparent and semitransparent wedges were examined for variation of the photoelectric current as thickness of the metal was increased. The metal was deposited on quartz by the evaporation method and examined when monochromatic light fell on the metal side of the plate.

The results are found to be consistent with the view that the probability of an electron going a given distance without losing its ability to escape falls off exponentially with the distance, when this distance is less than about 40 $\mu\mu$. Up to this thickness there is a parallelism between optical absorption and photoelectric emission. For large wave-lengths this parallelism is more pronounced than for short wave-lengths. For greater wave-lengths optical absorption may increase but photoelectric emission decreases terminating at the threshold value of photoelectric sensitivity.

The results seem to support the view that photoelectric emission is probably not caused by the direct absorption of energy out of the incident light beam, the light only acting as the agent which sets the electron free from its parent atom.

THE UNIVERSITY OF NORTH CAROLINA.

16. FREE MODES OF OSCILLATION IN LOOP AËRIALS.

BY S. L. BROWN AND C. P. BONER.

LOOPS with the turns widely separated have been investigated to ascertain their free modes of oscillation when excited by a spark in the loop circuit, by damped oscillations in a circuit loosely coupled with the loop, and by undamped oscillations. The results show that a loop has several free modes of oscillation when excited by a spark in the loop circuit and that the higher modes have no simple relation to the lowest or fundamental mode. The intensity of these modes of oscillation may be altered by adding capacity across the terminals of the loop but this capacity affects the frequency of the lowest or fundamental mode only, to any appreciable extent. When a loop is excited by damped oscillations in a nearby circuit, it will respond to several different frequencies of the exciting current, but these different resonant frequencies are changed by adding capacity across the terminals of the loop. When the loop is excited by undamped oscillations in a nearby circuit, it will respond to several different frequencies of the exciting current, but the intensity and frequency of the several resonant oscillations are changed by adding capacity across the terminals of the loop.

UNIVERSITY OF TEXAS.

17. IMPROVED EXPERIMENTS ON MAGNETIZATION BY ROTATION.

BY S. J. BARNETT AND L. J. H. BARNETT.

SINCE the report of Dec., 1920, more than two thousand observations have been made on iron, steel, nickel, cobalt, and Heusler alloy. To reduce errors from speed, spiral gears have been substituted for belt and pulleys. The magnetometer has been improved, and has been used altogether in four different positions. Small stellite journals, an agate bearing, and an improved process of demagnetization, together with a return to equatorial positions of the magnetometer, have been used to reduce the error from torsion. To reduce errors from eddy currents, a larger and better constructed frame has been used to compensate the main part of the earth's magnetic field; and extra coils, in conjunction with variometers, have been installed to compensate the variations. Other errors have been reduced or eliminated. A long-suspected systematic error has been found in the 1917 magnetometer observations, causing the results to differ considerably from those obtained by the method of electromagnetic induction in 1914 and 1915, now fully confirmed. Rotating any one of the ferromagnetic substances named at one revolution per second is equivalent to placing it in an axial magnetic field with intensity -3.5×10^{-7} gauss, within 10% or less. This result would be expected if a single type of negative magneton, with ratio of angular momentum to magnetic moment equal to m/e, one half that of a ring of electrons, were responsible for ferromagnetism. Abraham showed in 1903 that a superficially charged Lorentz electron in rotation has the moment and the momentum giving this ratio. If a ring of electrons is chiefly responsible for ferromagnetism, positive magnetons also participate. Important improvements are in progress.

CARNEGIE INSTITUTION OF WASHINGTON.

18. THE EFFECT OF A LONGITUDINAL MAGNETIC FIELD ON THE MECHANICAL PROPERTIES OF A VIBRATING NICKEL WIRE.

BY C. V. KENT AND B. J. BABBITT. INTRODUCED BY H. M. RANDALL.

A NICKEL wire is set in free longitudinal vibration in a magnetic field. The change of elastic modulus with field intensity (H) at various tensions is calculated from change in frequency as determined by the method of Lissajou's figures. The retraction is also measured. The results agree well in character and magnitude with those of Honda and Terada.

The decrement of vibration varies in a remarkable manner for different fields and tensions.

For a given tension, the changes in modulus and decrement, and the rate of change of retraction, reach maximum values at the same field intensity. For different tensions, these maxima occur at nearly the same value of magnetization intensity, but different field intensities.

UNIVERSITY OF MICHIGAN.

19. THEORY OF END-LOSS CORRECTIONS AND THEIR APPLICATION TO TUNGSTEN FILAMENTS IN VACUO.

BY A. G. WORTHING.

A SOLUTION has been obtained for the differential equation giving the temperature distribution in an electrically heated, uniform, cylindrical filament in vacuo near a cooling lead or support, which is applicable to both long and short filaments.

For long filaments those in which the cooling effect at any point depends on a single lead or support, it is found that, when temperatures are expressed in terms of the maximum central temperature and distances in terms of what might be called a reduced unit of length, a single curve suffices for any temperature distribution. The same is approximately true for resistivity, luminosity, thermionic emission, etc. Total corrections are similarly related.

For short filaments, those in which the cooling effect at any point depends on two leads or supports, it is found that similar relations hold for filaments with equivalent lengths.

For filaments having different cross sections, *e.g.*, ribbon or wire, it is found that equivalent filaments—those operating at the same temperature and wattage on the same voltage—suffer equal end-losses.

All three conclusions have been verified experimentally to within the uncertainties of measurement.

NELA RESEARCH LABORATORIES,
CLEVELAND, OHIO,
April, 1922.

20. EFFECT OF THE CURRENT DISTORTION BY LONG LINES ON THE OPERATION OF RECORDING RELAYS.

BY CARL KINSLEY.

THE arrival curve of a current impulse is distorted by a long line. It is seen from the Braun tube oscillograph shown that a recording device with any lost motion will give very inaccurate results. Extensive experiments by J. Zelisco have shown that with the principal relays in service a time interval of 0.002 to 0.005 second is needed to set the relay tongue into motion and from 0.004 to 0.006 second is then used before the record is made.

A relay which can be fitted to the circuit in which it is to be employed, which in use has satisfied all the requirements yet imposed and which makes an autographic record of its operations, has been recently developed and can be briefly described.

A schematic drawing shows the essential details. The tongue is composed of a stiff spring with a soft iron armature on its end. The natural period can be made as high as desired and should be considerably above that of the succession of impulses whose record is sought. The tongue is permanently magnetized—by a magnet or local current—and is normally held in a distorted position. The line impulse releases the tongue, with no time loss, and the record is made at an interval after the release, which can be exactly determined by computation as is shown by the graph giving frequency tests. The local circuit is closed through a moving chemically prepared paper strip which records the instant of contact, the time of which can be determined by a clock record made on the same strip. In the illustration the records of two such relays are given when operating at a speed of 0.005 second between strokes. No variation in operation within 0.0001 second is found on the record.

CORNELL UNIVERSITY,
March 30, 1922.

21. THE CALCULATION OF THE CAPACITY OF ANTENNAS.

BY FREDERICK W. GROVER.

FORMULAS have long been available for the calculation of the capacity of wires, where the length is very great compared with the radius of cross section and the distance between the axes. These conditions are not satisfied in the case of systems of wires such as are used for antennas. It is necessary in such cases to take into account the variation of the charge density along the wire resulting from finite length.

Formulas applicable to such systems have been published in recent years by Howe and Cohen. The former obtains the capacity by calculating the potential of the charge under certain assumptions as to the effect of the variation of the charge density; the latter makes use of the reciprocal relation between the linear inductance and capacity of the wires and formulas for the joint inductance of parallel circuits. Howe has pointed out the considerable differences between the values given by the two methods.

The present paper shows that the disagreement of the methods is only apparent and disappears if accurate inductance formulas are used. Simplified formulas are also obtained for calculating the capacity of a number of important arrangements of wires, including multiple systems, and tables are given which enable numerical results to be obtained with a minimum of labor.

Union College,
Schenectady, N. Y.

22. Direct Capacity Measurement.

By George A. Campbell.

The direct capacities of an electrical system with given accessible terminals are defined as the capacities which, connected across the terminals in pairs, will be the exact equivalent of the system in its external reaction upon any other electrical system with which it is associated only by conductive connections through the accessible terminals. Direct capacities are thus Maxwell's "coefficients of induction," with sign reversed, but they have the advantage of invoking the picture of a concrete network of condensers which is a realizable equivalent of the given electrical system. Direct conductances, admittances and impedances are defined in a similar manner. An individual direct capacity, the magnitude of which is required, cannot be removed and isolated from the other direct capacities in its own electrical system, but must be measured while still connected to them. Methods of measurements have, however, been devised which give a direct reading of the individual direct capacity. Of these methods, the one found to be most accurate, convenient and generally useful is a substitution method involving a particular connection of the terminals of the electrical system to the corners of an alternating current bridge containing variable capacity and conductance or their equivalent.

American Telephone and Telegraph Company.

23. The Complete Scale of Color Temperature and Its Application to the Color Grading of Daylight and Artificial Illuminants.

By Irwin G. Priest.

The scale of color temperature has been proposed by Hyde and his associates as a suitable scale for the color grading of illuminants, and considerable data on the color temperatures of artificial illuminants have been published.[1] The experimental methods used by Hyde and his associates for the determination of color temperatures have been restricted to temperatures below about 3200° K., *i.e.*, below the temperature of the arc and far below the various phases of daylight.

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[1] Hyde and Forsythe, J. Frank. Inst., *183*, pp. 353–354; 1917. Hyde, Forsythe and Cady,

The purposes of the present work have been to devise means for the color grading of daylight and artificial daylight as well as artificial illuminants in terms of color temperature and to establish a color-temperature scale from the color of the Hefner lamp to that of the blue sky (1880° to 24,000° K.).

Using the method of rotatory dispersion,[1] it has been found possible to determine the apparent color temperature of the various phases of daylight. It has been noticed, however, that the spectral center of gravity of light is a more suitable scale than temperature, since on it equal intervals indicate approximately the same color difference at all points on the scale, which is very far from true on a temperature scale.

The method is described, its sensibility, precision and accuracy are discussed, and experimental data on the apparent color temperature of daylight together with a diagram of the scale are given in a paper now in course of preparation.[2]

NATIONAL BUREAU OF STANDARDS,
April 1, 1922.

24. A SIMPLE AND ACCURATE METHOD FOR DETERMINING SURFACE TENSION AND DENSITY OF MOLTEN GLASS.

BY EDWARD W. WASHBURN.

Surface Tension.—The glass is contained in an electrically heated porcelain pot about 9 cm. in diameter and 15 cm. high provided with an electrically heated cover, in the center of which is a hole through which passes a platinum wire, on the lower end of which, just above the surface of the glass, hangs a platinum cylinder 4 cm. in diameter by 4 cm. high. The weight of the cylinder is borne by a sensitive coiled spring. The level of the lower end of the spring is read with a cathetometer and the furnace and pot are then gradually raised until the surface of the glass makes contact with the platinum cylinder and a second reading is taken with the cathetometer. The platinum cylinder is then pushed below the surface a short distance and allowed to rise to its equilibrium position. By this procedure the equilibrium position is found to be the same for the two directions of approach as closely as can be determined with a cathetometer. The platinum cylinder is standardized before and after each determination by similar measurements with liquids of known surface tension.

Density.—The density of molten glass is determined with the same apparatus,

PHYS. REV. (2), *10*, pp. 395–411; 1917. Forsythe, PHYS. REV. (2), *18*, p. 147; 1921. Hyde and Forsythe, Trans. I. E. S., *16*, pp. 419–427; 1921. Kingsbury, J. Frank. Inst., *183*, pp. 781–782; 1917.

[1] Cf. Priest, J. Op. Soc. Am., *5*, pp. 178–183; 1921. B. S. Sci. Papers, No. 417; 1921. J. Op. Soc. Am., Jan., 1922.

[2] "The Color Grading of Daylight and Artificial Daylight in Terms of Color Temperature by the Method of Rotatory Dispersion," *Sci. Pap., Bureau of Standards.*

but with a platinum sphere substituted in place of the platinum cylinder. The largest source of error in the measurements is that arising from the variability of the temperature.

Results.—The results show that the surface tension of the soda-lime-silica glasses between 1200° and 1450° C. is of the order of magnitude of 150 dyne/cm.

University of Illinois.

25. New Proof of the Specular Reflection of Molecules.

By R. A. Millikan and Karl S. Van Dyke.

The results obtained by one of the authors in previous studies by the oil-drop method have now been fully confirmed by measurements made on the coefficient of slip by the constant-deflection method using gases at low pressures enclosed between concentric cylinders, one of which is rotated at constant speed. The fraction of the impinging molecules which are specularly reflected and the fraction diffusely reflected are determined for different gases and different surfaces and the results found in complete agreement with the results previously found by the oil-drop method.

California Institute of Technology.

26. Radial Flow in Rotating Liquids.

By Harold Mottsmith and Irving Langmuir.

Zocher has observed that when a colloidal solution of vanadium pentoxide in a beaker is given a rotary motion and examined vertically between crossed nicols, a dark cross appears whose arms, however, are not parallel and perpendicular to the plane of polarization, but are displaced 10° to 20° backward against the direction of rotation. It is now shown that this hitherto unexplained displacement is due to a radial component of flow arising from unbalanced centrifugal forces. The liquid near the bottom moves slowly because of viscosity. The more rapid rotation of the free surface causes an outward flow at the top and corresponding inward flow at the bottom. Because of the greater shearing stress at the bottom the double refraction due to the inward radial flow predominates and causes the observed shifting of the cross. A striking demonstration of the radial flow is also furnished by the settling of a precipitate from a liquid in a beaker. If the *solution* is rotated in a stationary beaker the precipitate settles in the center, but if the *beaker* containing a quiescent liquid is suddenly set into steady rotation the precipitate settles near the outer walls.

Research Laboratory, General Electric Co., Schenectady, N. Y.

27. Noises in Stressed Metals.

By Barry MacNutt and A. Concilio.

A sensitive microphone was attached to test specimens of Sb, Bi, Cd, Sn, Zn, and steel. The specimens were stressed in a testing machine and the loads at which noises were heard noted. The load at which the first noise was heard was quite constant for a given material and occurred in the neighborhood of the yield point.

LEHIGH UNIVERSITY.

28. THE SIMPLE RIGIDITY OF A DRAWN TUNGSTEN WIRE AT INCANDESCENT TEMPERATURES.

BY WILLIAM SCHRIEVER.

THE simple rigidity of a 10-mil drawn tungsten wire was determined at temperatures between 1000° and 2000° K. A static method was employed. By applying the same torque to both a short length and a long length of wire —middle portions of both lengths at the same temperature—it was possible to get the angle of twist of a section of the wire, all of which was at a uniform temperature. The torque necessary to produce the twist in the heated wire was measured by the twist in a fine cold tungsten wire of known constants. The temperatures were measured by means of an optical pyrometer of the Morse type; corrections were made for the absorption of the evacuated glass tube which enclosed the wire.

The modulus of simple rigidity for an equiaxed wire was found to be 21.7×10^{11} dynes/cm.^{2} at 1000° K. and only 3.1×10^{11} dynes/cm.^{2} at 2000° K. There was a relatively small decrease in the rigidity modulus between room-temperature and 1100° K. At a temperature (1600° K.) where the rigidity of tungsten was equal to that of steel at room temperature, the elastic limit of the tungsten was, relatively, extremely small.

Jeffries'[1] work on the change of crystal structure of tungsten wire by heat-treatments at various temperatures makes it possible to draw the following conclusions from the temperature-rigidity curves of the 10-mil tungsten wire:

1. The rigidity of an equiaxed tungsten wire is greater than that of a freshly drawn wire, both measurements being made at the same temperature.
2. Heat treatment in the grain-growth region causes an increase of rigidity at temperatures between 300 and 2000° K., and probably at all temperatures. Increase in grain-size causes an increase in the rigidity modulus.

Moduli of rigidity, as given in tables of physical constants, have, in general, been obtained from angles of twist which were not great enough to cause the elastic limit of the material to be passed. In the writer's research, the angles of twist were less than 0.10 degree per centimeter length of hot wire and yet, at the higher temperatures, this was considerably beyond the elastic limit. The readings of the angles of twist were made so quickly that the results calculated from them are very similar to those which would have been obtained if a torsion pendulum of a very small period had been used. It is suggested that the moduli of rigidity calculated from such observations be called moduli of "Instantaneous Rigidity."

PHYSICAL LABORATORY,
STATE UNIVERSITY OF IOWA,
July, 1921.

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[1] "The Metallography of Tungsten," Trans. Am. Inst. Mining Eng., pp. 1037–1092, 1918.

29. The Reversible Inductivity of Rochelle Salt under High Frequency Fields.

By John G. Frayne.

Reversible inductivity K is defined as $\Delta E \doteq 0(-\Delta D/\Delta E)$, D being the induction and E the electric field in the dielectric. A plate of the crystal cut with its faces perpendicular to the axis of greatest piezo-electric activity was used as the dielectric of a condenser. The capacity was determined by a resonance method using a field of two million cycles per second as the exciting source. The value of K is about one tenth the dielectric constant as measured by D.C. methods. The variation of K with temperature was obtained between − 80° C. and + 50° C. It increases from − 80° C. up to a maximum of − 20° C., then decreases to a minimum about 4° C., and increases again to a maximum at 23° C., and then decreases until the melting temperature is reached. The concave region of the curve coincides with the range of greatest piezo-electric activity. The dielectric constant as measured at D.C. varies in the opposite manner between − 20° and + 23° C.

The quantity K was measured for different states of polarization of the crystal. The high frequency e.m.f. was superimposed on the D.C. field. Different samples of the crystal used showed permanent polarization effects. The crystal became conducting and the capacity infinite for smaller field strength in one direction than in the other.

University of Minnesota.

30. Reciprocal Diffraction Relations between Circular and Elliptical Plates.

By John Coulson and G. G. Becknell.

Since the time of Poisson and Arago it has been a well-known phenomenon in light that, in the case of a point source, a bright circular spot exists at the center of the geometrical shadow of a disc placed perpendicular to the wave normal. But attention seemingly has not been called to the succession of diffraction patterns appearing in the shadow when the disc is rotated about an axis in it's own plane, nor to the reciprocal figures produced by ellipses.

A series of photographs made by a disc inclined at angles varying from 0° to 60° have been prepared. These illustrate the gradual change from the circular spot into an upright cross and thence into a series of broadening diamond-like figures with concave sides.

At any particular inclination of the circle an apparently identical figure may be produced by a thin ellipse, whose minor axis equals the diameter of the disc, cut from a circular cylinder at the same angle of inclination and placed perpendicular to the wave normal. An ellipse similarly cut, but with its major axis equal to the diameter of the disc, produces a contracted figure of the same shape. When an ellipse is rotated till its shadow is a circle the Arago spot is produced at its center.

The typically quadrantal character of the diffraction figure has drawn attention to the fact that each quarter of it is due to light from a particular quadrant of the circular disc or ellipse. This is analyzed in a number of photographs shown in the paper in which light is excluded from certain portions of the edges of these discs.

These figures have been found to be the evolutes of the corresponding geometrical shadows.

UNIVERSITY OF PITTSBURGH,
PITTSBURGH, PA.

31. A FLOW CALORIMETER FOR MEASURING THE HEAT CAPACITY OF GASES.

BY H. F. STIMSON, T. S. SLIGH, AND N. S. OSBORNE.

THIS instrument, though intended primarily for ammonia, is designed to measure the heat capacity of gases at pressures up to 75 atmospheres and temperatures below 150° C. The design is based on a well-known principle which has been used by numerous experimenters. The method is to observe the temperature rise produced by measured electric power in a steady stream of gas traversing the instrument at a measured rate.

Certain refinements have been attempted with the object of limiting size and heat capacity, securing thermal sensitivity, minimizing thermal leakage, and controlling experimental conditions which affect steadiness. Accessory apparatus includes stirred thermoregulated liquid baths, automatic pressure regulator, orifice flow-controller, pressure manometers, vacuum pumps, etc.

The calorimeter has been used for measurements on ammonia at temperatures from $-15°$ C. to $+150°$ C. and at pressures from 0.5 atmosphere to 20 atmospheres. Measurements have been made with rates of gas flow ranging from 0.3 gm./min. to 3 gms./min., power input from 0.1 watt to 1 watt, and temperature rises from 4° C. to 50° C. Measurements can usually be begun within an hour after starting the gas flow. Over 75 measurements of C_p of superheated ammonia vapor in the above range with various flows and temperature rises indicate an order of precision of 0.1 per cent.

BUREAU OF STANDARDS,
April 4, 1922.

32. ELASTIC CONSTANTS OF RODS AT HIGH FREQUENCIES.

BY W. G. CADY.

IN previous papers a method of setting a metallic rod into high-frequency longitudinal vibration has been described, the driving force being derived from small plates of a piezo-electric crystal cemented to the sides of the rod at its center. A high-frequency alternating electric field is impressed upon the crystal plates by means of an oscillating triode, causing alternating mechanical stresses which in turn are transmitted to the rod. In the present investigation this method is applied to the determination of Young's modulus for various metals and for glass, at frequencies from 15,000 to 100,000, and for quartz, in a direction perpendicular to the optic and electric axes, at frequencies from 100,000 to 2,000,000.

By applying the theory of longitudinal vibrations in rods[1] to data obtained with the above-mentioned resonators by means of a sensitive thermo-element, it has been possible to obtain provisional values for the coefficients of viscosity of different substances at high frequency, and to study the dependence of coefficient of viscosity upon frequency.

Wesleyan University,
Middletown, Conn.,
March 5, 1922.

33. The Influence of the Surface Tension on the Efflux of a Liquid in Jet-form.

By Julius Hartmann, Dr.Tech. Introduced by Hugo Fricke.

Because of the influence of the surface tension, the velocity of a liquid jet is modified from that found by Torricelli's law, and is given by the expression

$$V^2 = \left[\frac{\pi}{4} k^2 d^2\right]\left[h - \frac{1}{Pg} \cdot \frac{2C}{d}\right] 2g,$$

where V = the velocity = the volume of the outflowing liquid per second,
d = the diameter of the jet,
k = the co-efficient of contraction of the jet,
h = head,
p = specific gravity of liquid,
c = capillary constant.

An experimental arrangement for the verification of this formula has been made and the above formula is found to hold good for mercury and for water. The method furnishes a means of accurately measuring the capillary constant. The values found have been:

Water C = 74.0 dynes/cm. at 10° C.
Mercury C = 536.0 dynes/cm. at 16° C.

The Royal Technical College,
Copenhagen.

34. A Study of the Luminous Discharge in Hydrogen and in Mercury and a New Method of Measuring Ionization Potentials.

By George E. Gibson and W. Albert Noyes, Jr.

The luminous discharge in mercury and in hydrogen at various pressures was studied in tubes of various dimensions using heated tungsten cathodes.

If the discharge is started in such a tube and the potential between anode and cathode is then diminished, the discharge disappears suddenly at a voltage which is reproducible, provided the temperature of the cathode is sufficiently high. The value of this disappearance e.m.f. was found in hydrogen to be nearly a linear function of the pressure at high pressures. When the pressure is diminished below a certain value, depending upon the dimensions of the tube, the linear relationship between E and p ceases to hold, E diminishing less rapidly with the pressure and coming to a minimum, $E_{\text{min.}}$, at a value of p depending upon the dimensions of the tube.

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[1] Phys. Rev., *19*, p. 1, 1922.

If the length between anode and cathode is gradually increased in a tube of given diameter, $E_{\text{min.}}$ remains nearly constant at the ionization voltage, (30.8 for hydrogen and 10.6 for mercury) until at a limiting value of the length $E_{\text{min.}}$ rises abruptly to twice the ionization voltage, remains constant at this value over a further range of length, then rises abruptly to three times the ionization voltage and so on.

UNIVERSITY OF CALIFORNIA.

35. EXCITATION OF THE SPECTRA OF HYDROGEN AND OF NITROGEN IN LOW VOLTAGE ARCS.

BY O. S. DUFFENDACK.

Hydrogen.—In a two-element tube the lines and bands appeared with the arc, but the bands did not appear when the gas was dissociated in the tungsten furnace. This is additional evidence that the lines are due to the atom and the bands to the molecule.

Nitrogen.—The first positive bands appeared with the arc and increased in intensity with the voltage. The second positive bands appeared with the arc and decreased in intensity with increased voltage. At potentials above 70 volts the arc turned into a brilliant "flare" with enormously increased conductivity. The second positive bands appeared along with the spectrum of tungsten. This was explained on the basis of the formation of "active" nitrogen. The negative bands appeared a volt or two above the ionizing potential and increased markedly in intensity. Three bands not previously reported were observed at 5075, 5018, and 4961 Å. Only four lines were observed, 5003, 5006, 5667, and 5680, and these never below 70 volts. The probability that these are enhanced lines was discussed.

It was concluded that the positive bands are due to the neutral molecule, the negative bands to the ionized molecule, and the lines to the atom; and that the molecule is ionized without dissociation.

PRINCETON UNIVERSITY.

36. THE RELATIVE INTENSITIES OF STARK EFFECT COMPONENTS IN THE HELIUM SPECTRUM.

BY JOHN STUART FOSTER.

A modified Lo Surdo tube was used with its axis perpendicular to the slit. The Stark effect components were *separate* and *parallel.*

The relative intensities of the p and of the s components of He 4922, 4472, and 4388 in an electric field of 15,000 v./cm. were measured by means of a neutral wedge. The p and s components in turn illuminated the slit of a large glass spectrograph. Energy distribution curves were calculated from the contour of the images and the corresponding wedge densities. The gas pressure was 2.8 mm.; the voltage on the tube 6000 v.; the current 3 mil. amps.; and the plates were exposed for 8 hours. The results for the main p components follow in order of increasing wave-length: for the line 4388, 8.2,[1] 4.1, 19.2, 28.0; for 4472, 168, 694; for 4922, 9.7, 31.6. Corresponding results for the s components are: for 4388, 1.0,[1] 3.0, 11.3, 9.5; for 4472, 76, 464; for 4922, 6.2, 21.4.

At present the method is limited in its usefulness by the appreciable pitting of the cathode, which occurs during long exposures. The investigation is being continued.

Yale University.

37. Cathodolyminescence of Heated Alumina.

By D. T. Wilber.

It is found that ordinary powdered alumina built up into a fritted cone in the oxyhydrogen burner, when freshly prepared, shows colored bands under cathode rays. The individual spectra causing these are the red ruby lines, a green, a blue and an orange band. The ruby bands are due to alumina with minute traces of chromium, for a clear white synthetic sapphire showed a brilliant red cathodoluminescence. A mixture of alumina and magnesia in molecular proportions with one per cent. of manganese gave a brilliant green band. Alumina and lime with manganese as active metal gave a broad band in the yellow and green. Alumina and lime with copper gave a band in the blue.

The layers of color on the cone seem to be due to the fact that the various colors come out at various temperatures and are destroyed at other higher temperatures. The green develops at the lowest temperature about 900° and disappears at about 1300° C. The ruby red appears soon after the green and persists through melting. The blue appears near the melting-point. These effects are much reduced if the material is completely fused.

Cornell University.

38. Radiation from Oxides. I. Emissive Power of Zirconium Oxide.

By W. E. Forsythe.

The emissive power of zirconium oxide for red radiation ($\lambda = .665\ \mu$) has been measured by two methods. The first consisted of heating on a platinum strip a small piece of the oxide, which had been baked at a temperature of about 1800° K. and measuring the relative brightness of the oxide and the platinum strip. From these measurements both the temperature and emissive power can be calculated.

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[1] "Isolated."

The second method consisted in pressing the oxide in the form of hollow glowers and then making a small radial hole, from which the true temperature could be determined. This is the method used by A. G. Worthing of this laboratory in determining the emissive power of tungsten.

The results showed a rather wide range with an average of about 16 per cent. which does not appear to vary greatly within the temperature range (1600° to 2600° K.).

NELA RESEARCH LABORATORIES,
CLEVELAND, OHIO,
April 5, 1922.

39. VARIATION OF CONTACT DIFFERENCE OF POTENTIAL WITH TEMPERATURE IN POTASSIUM AND SODIUM, AND THE ACCOMPANYING CHANGES IN PHOTO-ELECTRIC EMISSION.

BY HERBERT E. IVES.

IF a tungsten filament is mounted in the middle of a highly evacuated glass bulb, whose walls are covered with a layer of distilled potassium in contact with an electrode through the glass, it is possible, upon raising the filament to incandescence, to obtain a thermionic current between the filament and the potassium. The voltage-current relation is of the usual type. If now the bulb is immersed in liquid air, it is found that the thermionic voltage-current curve is laterally shifted by a fraction of a volt, indicating that the potassium has become electronegative compared with its room temperature condition.

According to present photoelectric theory a change in the contact difference of potential should be accompanied by a shift in the photoelectric threshold, which in turn may be expected to go along with a change in the total photoelectric emission. Such a shift in the long wave limit, and a corresponding change in the total emission, are actually found. The photoelectric current is diminished upon dropping to liquid air temperature to about 80 per cent. of its original value, for blue light, and to progressively lower values in the green and yellow. Most of the change occurs below zero Centigrade, which fact, together with the preponderance of sensitiveness in the blue region where the effect is least, probably explain the previous failures to observe a dependence of the photoelectric effect on temperature. The same phenomenon is found to a lesser degree in sodium.

RESEARCH LABORATORIES, AMERICAN TELEPHONE AND TELEGRAPH COMPANY
AND WESTERN ELECTRIC COMPANY, NEW YORK,
March 31, 1922.

40. A PRECISION ROTATING SECTOR: APERTURE VARIABLE AND MEASURABLE WHILE IN MOTION.

BY A. H. PFUND.

THE outstanding defect in the well-known rotating sector whose aperture is variable while in motion lies in the mechanism for reading the angular opening. Due to the unavoidable "lost motion," the readings obtained from a scale over which a lever handle (whose motion is transmitted by clutches, gears, etc., to the sectors) moves, do not indicate the true angular openings of the sectored discs with precision.

This difficulty is overcome by means of a new stroboscopic device which makes possible the reading of graduated scale engraved on the rotating sectors. A narrow slit is cut into one of the two discs near the fiducial mark. The light from a small incandescent lamp passes through this slit and falls on a concave mirror which focuses a sharp slit image on the fiducial mark and on the adjacent portions of the graduated scale (engraved on the second disc). A central opening, fitted with a magnifying lens, is cut into the concave mirror for purposes of observation. The angular opening is varied by a mechanism resembling that employed by Abney and others. When the sectors are rotated rapidly, the scale appears to be absolutely at rest. Even minute imperfections in the scale are depicted with astonishing clearness.

A further novelty lies in the sectored discs themselves. They are so cut as to present two adjacent fields of view. As the angular opening is varied, one field increases in brightness while the other decreases. In extreme positions, one field is black while the other is at maximum brightness—conditions are reversed as the sectors rotate, relatively, through 90°.

JOHNS HOPKINS UNIVERSITY,
March, 1922.

41. SPECIFIC INTENSITY OF RADIATION IN AN ABSORBING MEDIUM.

BY LEIGH PAGE.

IN 1882 Kirchhoff showed that the specific intensity of radiation in a transparent medium, multiplied by the square of the phase velocity, should be the same for all media in thermal equilibrium with one another. In his book on heat radiation Planck assumes this relation to hold for absorbing media. Laue has questioned this assumption and published an analysis of the problem (1910) which seems to show that the real part of the index of refraction should be replaced by the modulus.

In Laue's paper, it is assumed that a train of plane waves incident internally on the smooth surface of an absorbing medium, and the reflected train, can be treated as separated entities insofar as the propagation of energy is concerned. This, however, is not permissible, on account of the change in phase occurring on reflection. A more detailed investigation of the problem confirms Planck's assumption for moderately absorbing media. For strongly absorbing media it is doubtful if the substitution of trains of plane waves for the irregular radiation due to absorption and subsequent emission is legitimate.

YALE UNIVERSITY.

42. PHENOMENA IN GASES EXCITED BY RADIO FREQUENCY CURRENTS.

By E. O. HULBURT.

THE spectra from hydrogen, oxygen and air excited by currents of the frequency of the order of 10^6 alternations per second produced by an oscillating fifty-watt electron tube were photographed with a grating spectrograph in the spectral region from 5000 Å. to 3500 Å. These spectra were found to be identical with the spectra of the same gas stimulated by sixty-cycle current of the same strength as the radio frequency current.

The potentials just sufficient to set up luminosity in hydrogen and in oxygen were measured for direct and radio frequency, *i.e.*, frequencies from 10^5 to 10^7, current using electrode distances from 5 to 30 mm. and gas pressures from 1 to 5 mm. of mercury. For a specified gas pressure and electrode distance the direct potential and the maximum value of the radio frequency potentials were found to be the same. In the light of this result theoretical consideration indicated that the luminosity was started by collisions of electrons rather than of gaseous ions, with the gas molecules.

The flashes of light from hydrogen, oxygen, argon and air in turn excited by damped radio frequency current were found to be each a train of radio frequency flashes when examined by means of a rotating mirror. For hydrogen and argon the first few flashes of the radio frequency train showed a predominance of the green and blue lines of the spectrum, the later flashes of the train showed a predominance of the red lines. This was ascribed to the fact that the maximum value of the current in the first few cycles of the damped discharge was much greater than in the subsequent cycles.

STATE UNIVERSITY OF IOWA,
March, 1922.

43. ON THE EFFECT OF SHORT ELECTROMAGNETIC WAVES ON A BEAM OF ELECTRONS.

By C. J. LAPP.

MUCH has been written concerning discontinuous wave fronts of electromagnetic radiation. Sir J. J. Thomson and A. Einstein have definitely developed such theories. As an experimental test apparatus[1] was devised by means of which electrons were shot through a compact beam of radiation such as ultraviolet light or x-rays. In order to magnify any possible effect the electron beam was twisted into a long spiral of about 3 cm. pitch and 1.5 cm. mean diameter by means of a strong magnetic field. The helical beam thus formed was about 70 cm. long, and the path of each individual electron much longer. If the electron beam appeared continuously and it was permitted to fall on a photographic plate, traces made on the plate when the radiation was turned off should be different from those made when the radiation was present if any effect occurred.

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[1] Knipp, C. T., PHYS. REV., Vol. 34, p. 477.

The experiment was performed, using as a source of electrons an especially prepared Wehnelt Cathode of microscopic size described in the "Transactions of the Illinois State Academy of Science," Vol. 14, 1921. Due to the velocity distribution of the electrons in the beams, the traces made on the photographic plates were almost circular. Photographs were taken, first, of the electron beam alone, and second, of the beam when intense radiation was directed across its path near the electron source.

A long series of exposures taken when ultraviolet light was used as the radiation, showed a slight scattering of the electrons which was but little larger than the experimental error.

When hard x-rays were used as radiation, a marked effect was found. The exposures taken when the electrons had passed through the x-rays showed a distinct scattering effect. This is undoubtedly evidence in favor of a discontinuous wave front theory.

UNIVERSITY OF ILLINOIS.

44. EFFECT OF THE INITIAL EMISSION VELOCITIES OF ELECTRONS ON THE MINIMUM ARCING VOLTAGE IN GASES.

BY K. T. COMPTON AND Y. T. YAO.

THE maintenance of arcs at considerably less than half the minimum ionizing potential[1] is a fatal objection to the theory of low voltage arcs as due to cumulative ionization[2] unless the difference between the theoretical and observed voltage can be accounted for as due to initial velocity of emission of electrons from the cathode.

Minimum Striking Voltage.—It is shown that the observed striking voltage should be equal to the difference between the minimum ionizing and radiating potentials, *less* the average energy of emission of electrons from the cathode, in equivalent volts.

Minimum Maintaining Voltage.—On the assumption that it requires the same number of electrons, with velocities exceeding the critical value, to maintain the arc as to cause it to strike, it is shown that the arc may be maintained at a voltage less than the striking voltage by an amount calculable from the relative increase of current when the arc strikes and the known distribution of velocities among the emitted electrons.

Comparison with Experiment.—Curves showing the relation between arc current and applied voltage at various vapor pressures and cathode temperatures in mercury vapor, agree with the above theory within the limits of experimental accuracy.

PRINCETON UNIVERSITY.

45. THE EFFECT OF LIQUID SURFACE UPON THE ARCING VOLTAGE IN MERCURY VAPOR.

BY Y. T. YAO.

Low voltage arc in mercury vapor was studied under identical conditions for the two cases: (1) when the vapor was near the liquid surface, and (2) when it was far removed from it.. It was found that there was an essential difference in the value of the striking voltage. In the first case, the 4.9-volt arc was prominent, whereas in the second case the 6.8-volt arc was apparently the only one present. It is suggested that the same entities which are active in fluorescence and resonance may also be responsible for the 4.9-volt arc in mercury vapor, since R. W. Wood has shown that fluorescence and resonance are excited in mercury vapor by the 2536 Å. line only when the vapor has been freshly distilled from the liquid surface.[1] Experiments along these lines are in progress.

PRINCETON UNIVERSITY.

46. MOBILITIES OF ELECTRONS IN HYDROGEN.

BY LEONARD B. LOEB.

IN a recent paper published in the PHYSICAL REVIEW[2] the writer gave the results of the measurement of the mobilities of electrons in nitrogen. This work has been extended to H_2 with a considerable improvement in the oscillating system and an increase in the accuracy of the measurements. This increased accuracy led to an elimination of certain "ageing" effects which had distorted the voltage-mobility curves in N_2. It led also to the explanation of the asymptotic feet of the mobility curves in H_2 and N_2 as being due to the diffusion of ions formed between the plates, to the electrometer plate. It therefore became possible to eliminate these feet completely. As in N_2 it was found that the mobility constant reduced to 760 mm. pressure varied as a function of the field strength and pressure. The mobilities obtained are very closely given by the equation,

$$K = \frac{2.74 \times 10^6}{399 + \frac{V}{d}\left(\frac{760}{p}\right)^{3/4}} \tag{1}$$

or nearly as well by,

$$\left(K = \frac{1.905 \times 10^7}{81.3 + \frac{V}{d}\frac{760}{p}}\right)^{3/4}, \tag{2}$$

where V is the potential difference of the alternating potential in volts, d is the distance between the plates, and p the pressure in mm. of Hg. The difference in the shape of the curves given by equations (1) and (2) is very slight.

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[1] R. W. Wood, Astrophys. Jour., Vol. LIV., p. 149, 1921.

[2] L. B. Loeb, PHYS. REV., Vol. XIX., No. 1, pp. 224–38, Jan., 1922.

The fit of the curves is perhaps a trifle better in the case of equation (2), while (1) reproduces the family of curves more accurately. The form of the equation for mobility in H_2 differs from that observed in N_2 in that it has the power 3/4 instead of 1, as was originally found for N_2. Indications are that when the measurements are made in N_2 with the same precision as that achieved in H_2, the equation for the mobility in N_2 will be similar to the one in H_2. The new equation obtained in H_2 is more nearly of the form to be expected on theoretical grounds than the one found for N_2. It still however indicates that either the mean free path of the electron or the elasticity of the electron impact is a function of its velocity.

The values of K found for H_2 are in general much lower than the corresponding values found for N_2. If the values of K be taken for $V = 0$, *i.e.*, for electrons in thermal equilibrium with the gas molecules, the value of $K = 6860$ cm./sec. volt/cm. is obtained. The value of K computed from the theoretical equation for electron mobility in H_2, where $V = 0$, is $K = 13{,}060$ cm./sec. volt/cm. This indicates that the mean free path of electrons in H_2 is 0.53 of the value assumed by the kinetic theory of gases. Such a decrease in the mean free path of electrons could be caused by the attractive forces exerted by the electrons on the gas molecules. In the case of N_2 the value of K observed was 3.9 times the theoretical value. This indicates an abnormally great mean free path in N_2 which is at present unexplained. It is perhaps similar to the abnormal mean free path found in argon, independently by Ramsauer,[1] H. F. Mayer,[2] and Townsend.[3]

Ryerson Physical Laboratory,
April 4, 1922.

47. The Electron Emission from Thoriated Tungsten Filaments.

By Irving Langmuir.

Heating a tungsten filament containing thoria to 2800° K. causes a small fraction of the thoria to be reduced to metallic thorium distributed throughout the filament. At 2100° K. the evaporation of thorium becomes negligible and with exceptionally high vacuum the thorium, by diffusion, forms an adsorbed film covering a fraction θ of the surface with a layer of thorium atoms. The electron emission is measured at 1300° to 1800° where no diffusion occurs.

Theory and experiment show that the logarithm of the emission is a linear function of θ and the changes in θ caused by heat treatment are given by

$$N_0 \frac{d\theta}{dt} = DC_1(1 - \theta) - \nu,$$

where N_0 = Number of thorium atoms per cm.^{2} when $\theta = 1$; D = Diffusion coefficient (cm.^{2} sec.$^{-1}$) of thorium in tungsten; C_1 = Concentration gradient at the surface (atoms of Th × cm.$^{-4}$); ν = rate of evaporation of thorium (atoms cm.$^{-2}$ sec.$^{-1}$) from a tungsten surface. Experiments show that

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[1] C. Ramsauer, Ann. d. Phys., 64, p. 513, 1921.

[2] H. F. Mayer, Ann. d. Phys., 64, p. 451, 1921.

[3] J. S. Townsend and V. A. Bailey, Phil. Mag., Vol. 43, No. 255, pp. 593–600, March, 1922.

$$\log_{10} D = 0.21 - \frac{20900}{T},$$

$$\log_{10} \nu = 7.76 - \frac{44500}{T}.$$

Thorium atoms evaporate from underlying thorium atoms at rates very high compared to that of thorium from underlying tungsten atoms. Only for small values of θ (less than 0.1) is ν proportional to θ. For θ = 0.2 to 0.3, ν reaches a maximum and then decreases slightly (about 20 per cent.) when $\theta = 0.9$.

RESEARCH LABORATORY, GENERAL ELECTRIC CO., SCHENECTADY, N. Y.

48. THE REMOVAL OF THORIUM FROM THE SURFACE OF A THORIATED TUNGSTEN FILAMENT BY BOMBARDMENT WITH POSITIVE IONS.

BY K. H. KINGDON AND IRVING LANGMUIR.

THE experimental tube contains a molybdenum cylinder *c* with closed ends, through which pass two thoriated tungsten filaments, *a* and *b*. The tube is filled to about 0.01 mm. pressure with the gas whose ions are to be used, and ions are formed by passing an electron current from *b* to *c*. The voltage between *b* and *c* is kept as low as possible, while *a* is kept at a relatively high negative potential to *b*, and can thus be bombarded with positive ions of any desired energy. The removal of Th from the surface of *a* by this bombardment can be studied from the change in the electron emission of *a*. He and Ne have been used.

Conclusions:—(1) Ne ions remove Th faster than He ions of the same energy.

(2) The amount of Th removed per second does not increase in proportion to the amount of Th on the surface, and is independent of the temperature.

(3) At 500 volts only about one He ion in 190 succeeds in removing a Th atom from the surface.

(4) The rate of removal of Th increases approximately linearly with the energy of the ions; and is proportional to the positive ion current.

RESEARCH LABORATORY, GENERAL ELECTRIC CO., SCHENECTADY, N. Y.

49. THE MEASUREMENT OF MAGNETIC FIELD STRENGTH BY MEANS OF ELECTRON TUBES.

BY ALBERT W. HULL.

THE following method of calibrating magnetic field coils has been in use in the Research Laboratory for the past two years:

A two-electrode tube of circular cylindrical symmetry is connected in multiple with a standard voltmeter, and in series with a high resistance and a source of voltage.

The electron tube is placed in the field and rotated until the voltmeter reading is a maximum. The direction of the field is then given by the direction of the axis of the tube, and its magnitude H by the voltmeter reading V, according to the equation

$$H = \frac{6.72}{R}\sqrt{V},$$

where R is the radius of the anode.

The readings are independent of both filament temperature and generator voltage within wide limits, so that any available power supply may be used; and can be relied upon, *without calibration*, to within 5 per cent. in absolute value, and to within ¼ per cent. for relative values over a short range. Fields from 20 to 500 gauss can be measured in this way by appropriate choice of resistance and voltage.

An alternative method is to connect an electron tube of any type in *series* with a voltmeter and source of voltage. Calibration is necessary. The range is from 10 to 500 gauss. By using a symmetrical tube and a polarizing field coil around on the tube, the range may be extended down to 1/10 gauss.

Research Laboratory,
General Electric Company,
Schenectady, N. Y.,
November 22, 1921.

50. A General Relation for Electron Emission from Metals.

By Saul Dushman.

On the basis of the Nernst Heat Theorem it has been shown that the vapor pressure of a monatomic substance is given by a relation of the form

$$\ln p = -\frac{L_0}{RT} + \frac{5}{2}\ln T + C. \qquad (1)$$

According to the quantum theory, C, the so-called chemical constant, may be calculated from the equation

$$C = \ln\left(\frac{lu\,(2\pi)^{3/2}k^{5/2}M^{3/2}}{N^{3/2}h^3}.\right) \qquad (2)$$

Tolman has applied equation (1) to electron emission, by using the value of C derived from the vapor pressure data for helium. Using equation (2) to calculate C, and applying equation (1) to electron emission, it can be shown that the *emission from any substance*, in amperes per cm.^{2}, is given by the relation

$$i = 60.2T^2\epsilon^{-b_0/T} \qquad (3)$$

where $60.2 = \frac{10}{C}\left(\frac{2\pi k^2 me}{h^3}\right)$

This equation is found to be in very satisfactory agreement with electron emission data obtained from pure tungsten, and unimolecular layers of thorium and calcium on tungsten. The following values of b_0 have been obtained for these metals.

W	51,500 ± 500,
Th	34,000 ± 500,
Ca	26,000 ± 1,000.

RESEARCH LABORATORY,
GENERAL ELECTRIC CO.,
SCHENECTADY, N. Y.

51. THE SECONDARY ELECTRON EMISSION FROM NICKEL.

BY C. DAVISSON AND C. H. KUNSMAN.

THE total number of secondary electrons emitted per primary bombarding electron has been measured for nickel for bombarding potentials V, up to 350 volts, by the same method employed by Millikan and Barber (Proc. Nat. Acad., Jan., 1921) for copper.

The emission factor has a value of 1.08 for $V = 350$ volts, and decreases to 0.32 for $V = 15$ volts, and then remains practically constant at 0.30 for all speeds to $V = 0$. While the bulk of the secondary emission from nickel is made up of slow-speed electrons, electrons of all speeds up to the speed of the primaries are to be found at all bombarding potentials. The presence of high-speed electrons have not in general been observed in the investigations on the emission from metals.

Apparently the emission at the lower voltages is due to the escape from the metal of primary electrons that may on the average have had a considerable number of elastic encounters with atoms in and near the surface of the target. At high voltages the high-speed electrons escape from the target as the result of single encounters between primary electrons and atoms.

RESEARCH LABORATORIES OF THE
AMERICAN TELEPHONE AND TELEGRAPH CO.,
AND THE WESTERN ELECTRIC COMPANY, INC.,
April 19, 1922.

52. AN EXPERIMENTAL METHOD OF TESTING THE EXPRESSIONS FOR LONGITUDINAL AND TRANSVERSE MASSES OF THE ELECTRON.

BY L. T. JONES AND W. C. POMEROY.

EXPRESSIONS for the longitudinal and transverse masses of the electron have been deduced by Lorentz-Einstein, Abraham, Bucherer-Langevin and Walker. An experimental method of testing these expressions is proposed making use of an electron stream from a hot filament cathode, the electrons being accelerated by the sinusoidal voltage from a high potential transformer; thus in the beam studied a large range of electron velocities is present. Each electron, upon acquiring its maximum velocity, enters an electrostatic field, between parallel horizontal plates, which is a constant fraction of and at all times in phase with the variable accelerating field. Coincident with this field is a constant magnetic field. These fields produce downward and sidewise deflections, respectively, which depend in magnitude upon the velocity of the electron. A curve is traced upon a photographic plate placed on the lower of the horizontal plates. This may be compared with the theoretical curves, which have been calculated for each of the four theories. A plot of the calculated curves indicates the possibility of confirmation of one of the theories. The experimental work is proceeding.

Department of Physics,
University of California.

53. Oil-Drop Experiments as Proof of the Invariance of Electric Charge.

By F. W. Loomis.

At the last meeting I pointed out[1] that the fact that all of Millikan's oil drops could be made electrically neutral within 1/1000 of an electronic charge showed that the charge on an electron is equal to that on a proton to within 1 part in 4×10^{17}. This is true for the electrons composing substances as diverse as mercury and oil. It follows that all electrons have, to this order of accuracy, the same charge; and since the electrons in different substances have widely different velocities, this serves as a confirmation of the relativity law of the invariance of electric charge. A rough calculation can be made of the limit set by these experiments on the possible variation of charge with velocity.

New York University.

54. Study of the Hydrogen Radiation in the Red and the Infra-Red.

By F. S. Brackett.

Hydrogen lines have been observed at wave-lengths $\lambda = 4.0^5\,\mu$ and $2.6^3\,\mu$ due, according to Bohr's theory, to an electron falling into the fourth from the fifth and sixth rings respectively—forming the *first two members* of a *new series.*

Lines have also been observed at wave-lengths $\lambda = 1.8^8\,\mu$, $1.2^8\,\mu$, $1.0^9\,\mu$, $1.0^1\,\mu$ and $0.95\,\mu$. These form the *first five members of the Paschen series*, due to an electron falling into the third from the fourth, fifth, sixth, seventh and eighth rings respectively. The first two were observed and accurately measured by Paschen.

The relative intensities of H_α and the first Paschen line are found to vary with the current. In some cases the first Paschen line was found to be more intense than H_α in the ratio 4 : 3. The first line of the new series was found to be about one fourth the intensity of H_α.

The *variation* of *intensity* of Hydrogen lines is *not a continuous function of current intensity. Discontinuities* occur for currents corresponding to the *threshold* (resonance) *potentials* predicted by Sommerfeld. Those have been

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[1] Paper 15, 113th meeting.

identified which ***correspond to*** amounts of energy necessary in order to expel an electron from the ***first*** to the ***third, fourth, fifth, sixth, seventh*** and ***eighth rings*** respectively, also probably the ninth, tenth, eleventh and twelfth rings. Other discontinuities have also been observed which would not be expected from theory.

Johns Hopkins University,
April 7, 1922.

55. The Voltage-current Relation in Central Anode Photo-electric Cells.

By Herbert E. Ives and Thornton C. Fry.

It is found experimentally that the voltage photo-electric current relation in central anode photo-electric cells is different for different colors. On the assumption that the electrons are emitted from the walls in all directions according to a cosine distribution, and with all velocities up to the limit set by the quantum relation, according to a parabolic distribution law of energies, a mathematical theory is developed. The electrons describe elliptic orbits, determined by their initial direction and velocity, and the electric field. It is shown that very small initial velocity differences are only overcome by large electric fields. For an assumed case of a threshold at 6000 Å.U. saturation is calculated to occur at 40 volts for emission due to 5500 Å.U. radiation, and at 160 volts for emission due to 4500 Å.U. radiation. These differences agree as to order of magnitude with the experimentally observed ones.

Research Laboratories, American Telephone
and Telegraph Company and Western Electric
Company, New York,
March 31, 1922.

56. The Broadening of the Balmer Lines of Hydrogen with Pressure.

By E. O. Hulburt.

Spectrograms were taken of H_β, H_γ and H_δ of hydrogen excited by condensed discharges for gas pressures from 2 to 135 mm. of mercury. At the highest pressure the photographic widths of the lines were nearly 100 Å. Throughout the series of pressures the intensity of the central portion of H_β was maintained sensibly constant. Assuming that the widening was caused by disturbance of the uniformity of the radiation due to collisions of the radiating particles (as proposed by others), the widening of the lines with pressure was calculated and found to be considerably less than that observed. This result indicated that the assumption was an improper one, and that the widening should be attributed to other causes, such as the effect of the electrical fields, as investigated by Merton (Proc. Roy. Soc., 92, 322, 1915).

State University of Iowa,
April, 1922.

57. Crystal Structures of Vanadium, Germanium and Graphite.

By Albert W. Hull.

Vanadium has been analyzed in powdered form by the x-ray diffraction photograph method. Its lattice is a body-centered cube with side 3.04 Å. The distance between nearest atoms is 2.63 Å, and the ideal density 5.96.

Germanium is found to have a crystal structure the same as that of diamond. The side of the unit cube is 5.63 Å, the distance between the nearest atoms 1.218 Å, and the density 5.36.

New and more accurate diffraction patterns of graphite have confirmed the structure described in an earlier paper, viz., a lattice of the hexagonal close-packed type. The measurements can not be reconciled with the rhombohedral structure found by Debye. The exact distance between nearest planes can not yet be stated with certainty. Measurements are in progress which, it is hoped, will determine this distance.

Research Laboratory,
General Electric Co.,
Schenectady, N. Y.

58. The Diffusion Coefficient in Solids and Its Temperature Coefficient.

By Saul Dushman and Irving Langmuir.

Consider a solid as consisting of layers of atoms, δ being the distance between layers. Let Kdt be the probability that a given atom in a layer A shall move into the adjacent layer B during the time dt. Then the diffusion coefficient is

$$D = K\delta^2. \tag{1}$$

The quantity K is a frequency analogous to the velocity constant of a unimolecular chemical reaction. The velocity of such reactions is approximately given by the semi-empirical relation

$$K = \nu e^{-h\nu/kT} \quad \text{or} \quad K = \frac{Q}{Nh} e^{-Q/RT}, \tag{2}$$

where ν or Q is characteristic of the reaction. It is now shown that this relation also holds for the K calculated by (1) from the diffusion coefficient. For the diffusion of thorium through tungsten at 2300° K. $D = 1.1 \times 10^{-8}$ cm.^{2} sec.$^{-1}$. Substituting this in (1) and (2) gives $Q_{\text{cal.}} = 90{,}500$ g. calories per g. molecule. Plotting log $D_{\text{obs.}}$ against the reciprocal of the temperature, from 1900 to 2500° K., gives a straight line from whose slope we get $Q_{\text{obs.}} = 94{,}000 \pm 3{,}000$, in satisfactory agreement with $Q_{\text{cal.}}$. Even better agreement is obtained from published data of Roberts-Austin on diffusion of gold in lead and of Warburg and Schulze on diffusion of sodium ions in glass. Thus the temperature coefficient of D may be calculated if the value of D is known at one temperature.

Research Laboratory, General Electric Co., Schenectady, N. Y.

59. NOTE ON THE COHN-MINKOWSKI FORMULA FOR THE MOTION OF INSULATORS IN A MAGNETIC FIELD.

BY S. J. BARNETT.

ON the theory of Lorentz and Larmor the polarization produced by the motional electric intensity acting on an insulator with dielectric constant K and permeability unity moving with velocity v in a magnetic field with induction B is

$$P_1 = \frac{(K-1)}{4\pi}\frac{1}{c}[vB].$$

If the permeability is μ and the intensity of magnetization

$$I = \frac{B}{4\pi}\left(1 - \frac{1}{\mu}\right)$$

there is in addition an electric polarization

$$P_2 = \frac{1}{c}[vI] = \frac{1}{4\pi c}\left(1 - \frac{1}{\mu}\right)[vB]$$

due to the magnetization. This follows from a simple theorem of Maxwell's: The motion with velocity v of a constant electromagnetic system with vector potential A produces an electric field the potential of whose polar part is $\varphi = (Av)/c$. An immediate consequence of this is that the electric moment of the distribution produced by the motion is equal to $1/c[vm]$, where m is the magnetic moment. Applying this to the unit volume, we obtain the above expression for P_2. The total polarization is

$$P = P_1 + P_2 = \frac{K}{4\pi c}\left(1 - \frac{1}{\mu K}\right)[vB],$$

a result hitherto obtained only on the theories of Cohn and Minkowski. The result, like Maxwell's theorem, is correct only to quantities of the first order in v/c. Reference is made to results obtained by Budde, Lorentz, and others, which are implicit in Maxwell's theorem, the approximate character of which is due to its being based on a principle of relativity assuming equality of electromotive intensity and magnetic induction to fixed and moving observers.

CARNEGIE INSTITUTION OF WASHINGTON.

60. A NEW METHOD FOR THE GENERATION OF SOUND WAVES.

BY JULIUS HARTMANN. INTRODUCED BY HUGO FRICKE.

IN an air-jet, produced by a pressure higher than 1.9 Atm., there is a peculiar, periodic distribution of the pressure along its length, a demonstration of which can be made photographically by means of a special optical arrangement. If the aperture of a small cylindrical acoustic resonator is introduced into the parts of the jet where the pressure is rising, a note is produced. The wave-length of this has been determined by a Kundt tube and is found to be determined by the equation

$$\lambda = 4l + 2.4d,$$

where l is the length and d the diameter of the resonator.

Notes of a frequency higher than 100,000 have been produced by means of this sound generator. The efficiency of the generator is about 10 per cent.

If the narrow aperture of a bulb is introduced in the jet, a note is also produced. The frequency of this note is mainly determined by the volume of the bulb, by the width of the aperture, and by the place in the jet where it is introduced. This method affords a very efficient siren.

THE ROYAL TECHNICAL COLLEGE,
COPENHAGEN.

61. THE EFFECT OF A MAGNETIC FIELD ON THE ABSORPTION OF X-RAYS.

BY JOSEPH A. BECKER. INTRODUCED BY F. K. RICHTMYER.

Effect of a magnetic field on the absorption of x-rays, if it can be measured, would have an important bearing on the theory of atomic structure. Since the effect is very small, a differential method was adopted and by eliminating various spurious effects the apparatus was made sensitive enough to detect a change of 1 part in 10,000. Observations were made with a peak voltage of 80 across the Coolidge tube (mean wave-length about 0.3 Å.) and with a magnetic field H of about 18,000 gauss. For H perpendicular to the rays, *aluminum, carbon, copper, iron, nickel, platinum, zinc, and silver* showed changes in absorption coefficients of $+8 \pm 6$, -5.6 ± 2, $+0.8 \pm 0.4$, -10 ± 2, $+1.6 \pm 0.5$, $+1.7 \pm 0.4$, -1.2 ± 0.4 and $+1.6 \pm 0.8$, parts in 10,000 respectively, while with H parallel to the rays the corresponding changes were $+2.7 \pm 1$, $+3 \pm 1$, $+1.4 \pm 1$, -0.5 ± 2, $+0.7 \pm 2$, $+1.1 \pm 1$ and $+1.3 \pm 1 \times 10^{-4}$, silver not being tried. These results are in accord with the hypothesis that the magnetic properties are largely determined by the outer shell or valency electrons, since at the wave-lengths used by far the greater part of the absorption is due to the inner electrons. Wood was also tested with softer rays having a mean wave-length of about 1.2 Å., and showed a change of $+80 \pm 20 \times 10^{-4}$ as compared with 3×10^{-4} for carbon for wave-length 0.3 Å. Following the suggestion of this result it is proposed to do further work with light elements and softer x-rays.

CORNELL UNIVERSITY.

62. FORMATION AND LIFE OF METASTABLE HELIUM.

BY FABIAN M. KANNENSTINE.

HELIUM arcs were formed between a Wehnelt cathode and nickel anode in a pyrex tube containing carefully purified helium. A voltage of about 35 volts from a battery was impressed between the anode and cathode. The electrical circuit was arranged so that the impressed voltage could be suddenly reduced. The arc current was passed through the deflecting coils of a sensitive Braun tube and the spot was examined directly and with a rotating mirror.

On suddenly reducing the voltage to a value below about 4 volts, it was seen in the rotating mirror that the arc was extinguished in a time too short to be so observed. When the lower voltage was increased to about 4 volts a sudden change occurred; the arc died out gradually in a time that could be readily observed, indicating the possibility of maintaining an arc in the metastable helium formed, with about 4 volts as long as any was present. With the lower voltage 22.6 volts the arc continued at a certain value for a brief time before dying out, while with 23.6 volts the arc current decreased in two stages, which is possibly connected with the fact of the existence of two radiating potentials in helium.

This interpretation in terms of the presence of metastable helium was also supported by Braun-tube oscillograms when the arc was excited by alternating electromotive forces of various frequencies. With 60 cycles the arc did not strike below the ionization potential of helium indicating that the metastable helium disappeared during the negative half of the wave. With 350 cycles the arc struck at about 4 volts showing that the metastable helium persisted during half a cycle.

The theoretical ionization potential of metastable helium is 4.8 volts and probably is to be identified with the value observed.

University of Chicago.

Second Series *August, 1922* *Vol. XX., No. 2*

THE

PHYSICAL REVIEW.

ON THE NATURE OF THE NEGATIVE AND POSITIVE IONS IN AIR, OXYGEN AND NITROGEN.

BY HENRY A. ERIKSON.

SYNOPSIS.

Positive and Negative Ions in Air, Oxygen and Nitrogen.—(1) *Mobilities just after formation* were measured by using a modified form of Zeleny's blast method. Ions produced in air by polonium rays were drawn immediately by a current of 470 cm./sec. into one side of a cross field of 130 volts/cm. and the distance they were carried along before they were dragged to the other side by the field was determined. When the average age of the ions was about 0.03 sec. the mobility was found to be the same for both positive and negative ions and equal to that for normal negative ions, about 1.89 cm./sec./volt/cm. As the age was increased to 0.5 sec., however, the positive mobility decreased to its normal value, about 1/1.40 times the negative mobility. The same results were obtained with dry commercial oxygen and nitrogen, except that the aging of the positive ion was more rapid in oxygen. (2) *Nature of the ions.* In explanation of the above results it is suggested that the negative ion and the initial positive ion are each one molecule in size and that the permanent positive ion is two molecules in size. This suggestion agrees with the view that when ionization occurs an electron is ejected from a molecule, leaving a positively charged molecule, an initial positive ion, which does not immediately acquire the second molecule needed to form a permanent positive ion. The electron attaches itself to a molecule and forms a permanent negative ion. It is also shown that the observed ratio of the mobilities for ions with one and two molecules respectively agrees with that computed according to the small ion theory of Wellisch.

THE nature of the positive and negative ions produced in air by an ionizing agent is a question of considerable interest. It has not been easy to obtain conclusive evidence.

In 1900 Zeleny[1] succeeded in determining the absolute values of the mobilities of the ions in question. The values found were, for the negative ion 1.87 cm./sec./volt/cm., and for the positive ion 1.36, giving the ratio of the negative mobility to the positive of 1.375.

Each of the above ions forms a stable unit. The ratio 1.375 shows that these units are not alike. To what this difference is due is a question of interest.

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[1] Phil. Trans. A, Vol. 195, p. 193.

About two years ago[1] it occurred to the writer to try a modified form of Zeleny's blast method.

The experimental arrangement was as indicated in Fig. 1. *A* and *B* were two parallel plates 5 cm. wide, 40 cm. long and 4.5 cm. apart. *C* was a plate about 12 cm. long placed about 0.6 cm. below *A*. *A* and *C* were connected. *D* was a narrow insulated strip placed in the plane of *B* and connected to a quadrant electrometer. The plate *B* and strip *D* were movable so that the down stream distance of *D* could be altered. The sides of the apparatus were of glass.

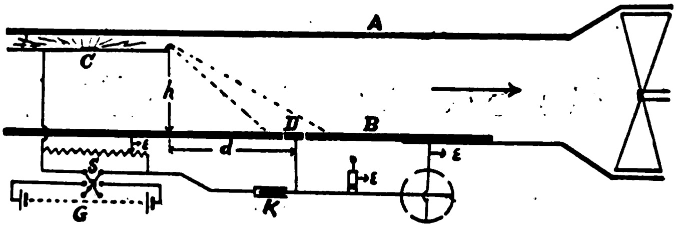

Fig. 1.

Air from the room was drawn through this rectangular tube by means of a fan driven by a synchronous motor. Plate *B* was kept at zero potential while *A* was raised to the potential of the battery *G*. In order to compensate for any change in the voltage of the battery *G* during readings the air condenser *K* was introduced.

A polonium plate was placed at *C*, the rays from which ionized the air between plates *C* and *A*. As *A* and *C* were connected there was no field causing the ions to move to the plates. The ions were carried by the air to the mouth of this chamber where they entered the field between *A* and *B*. If *A* were positive the positive ions were driven to *B*, and negative to *A*.

By changing the down stream distance of the strip *D* the current at the different points on *B* could be measured. For each position of the strip *D* both the positive and negative currents were measured by reversing *S* leaving the conditions otherwise unchanged.

The velocity of the air was obtained by means of an anemometer. The times for a given deflection of the electrometer for the positive and negative currents at different positions of *D* were obtained. Upon plotting the reciprocals of these times against the down stream distances of *D* as abscissæ, the curves shown in Fig. 2 were obtained:

To the writer's surprise these two curves were found nearly to coincide, indicating equal mobilities of the positive and negative ions. The average age of the ions in this case was of the order of 0.03 second.

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[1] Phys. Rev., (2) XVII., p. 400; (2) XVIII., p. 100.

The spreading of the curves is due primarily to the slant of the plate B with reference to the direction of the ionic stream. By projecting on a plane at right angles to the ionic stream the spreading is of the order of 3 cm. instead of 8 cm. The amount of spreading due to the self repulsion of the ions is, on each side, of the order of 0.5 cm., about the thickness of the current sheet. Deducting this will reduce the spreading to about 1.5 cm. which is undoubtedly due mainly to air turbulence. Excessive air turbulence was however not present. This was determined by means of smoke streams. The factors given above are of an order such as to preclude the necessity of attributing the spreading to non-homogeneous ions.

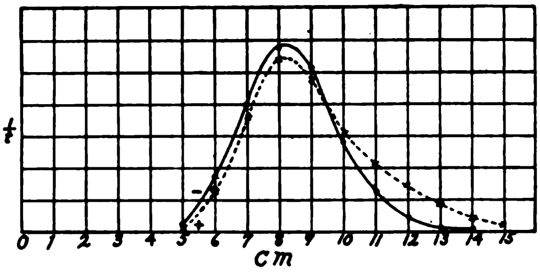

Fig. 2.

The absolute value of the mobility may be determined as follows: Let h be the average distance the ion travels at right angles to the stream of air and d the distance it travels down stream in the same time t. Then

$$h = k\frac{V}{H}t,$$

but

$$t = \frac{d}{v};$$

$$\therefore \quad k = \frac{hHv}{Vd},$$

where H = distance between the plates A, B,
V = difference of potential between plates A, B,
v = velocity of air,
k = mobility of ion.

The mobility k therefore varies inversely as the down stream distance d. The ratio of two mobilities therefore is

$$r = \frac{k_1}{k_2} = \frac{d_2}{d_1}.$$

If two ions have the same mobility their down stream distances *d* are the same.

As the curves for the positive ion and the negative ion came superimposed, the conclusion must be that both ions had the same velocity.

The next question of interest was to determine if the mobility represented by the maxima of the curves was the normal mobility for the negative or for the positive ion.

The following values for the quantities necessary for the determination of the mobility were obtained:

V = 535 volts,
d = 8.2 cm. (using maximum of curve),
h = 4.2 (using same average value for H),
v = 470 cm./sec.

The above values gives for the mobility

$$k = 1.89 \text{ volt/cm.}$$

As this is of the order of the normal value for the mobility of the negative ion, the necessary conclusion is that the positive ion involved had the same mobility as the normal negative ion.

In order to determine if the age of the positive ion had any effect an extension was added as shown in Fig. 3. The polonium plate was placed at *P* so that the ions were of the order of 0.5 second old when they entered the field at *B*. The air velocity remained the same as before.

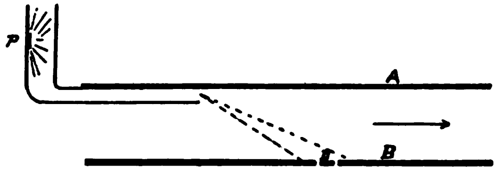

Fig. 3.

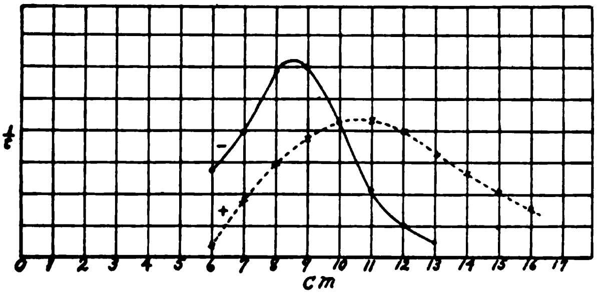

Fig. 4.

The curves obtained for the positive and negative ions are shown in Fig. 4. As the maximum for the negative ion remained unchanged it became evident that the poistive ion had undergone a change during the first fraction of a second of its life as its maximum had shifted down stream indicating a slower ion.

The same change was obtained when the ions were aged by reducing the velocity of the air, the polonium plate being at *C*, Fig. 1. The curves *A* and *B* in Fig. 5 were obtained in this manner. The ratio of the initial mobility to the final mobility is

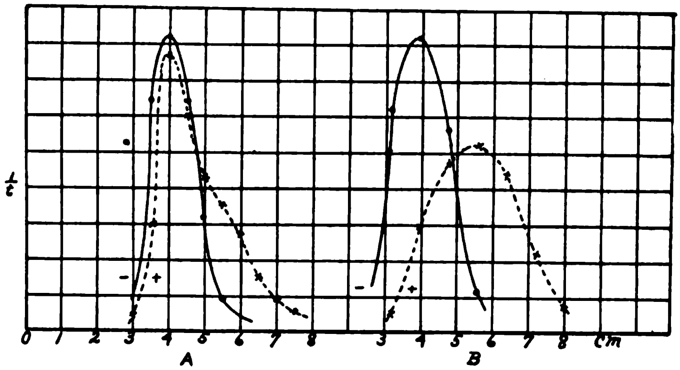

Fig. 5.

$$\frac{k_1}{k_2} = \frac{5.5}{3.9} = 1.40$$

which is about the normal ratio for air.

The significance of the above must be that the negative and positive ions are initially alike in magnitude and that the positive ion soon increases to a larger stable unit.

In order to determine if this effect is peculiar to air the apparatus was enclosed so that oxygen and nitrogen could be investigated separately.

The gases were obtained from commercial supply tanks and were dried by passing through $CaCl_2$. The gases were not of a high degree of purity. The ions were aged by reducing the gas velocity.

The curves obtained are given in Fig. 6.

The results obtained show that in oxygen and nitrogen, of the purity involved, the negative ion does not change. The positive ion, however, does in each case undergo a change. It is also observed that the change in the mobility of the positive ion in oxygen is somewhat more rapid than in nitrogen.

Statement of Hypothesis.—In explanation of the above it seems most reasonable to take the molecule as the unit in terms of which the change takes place. On this basis the simplest hypothesis becomes as follows:

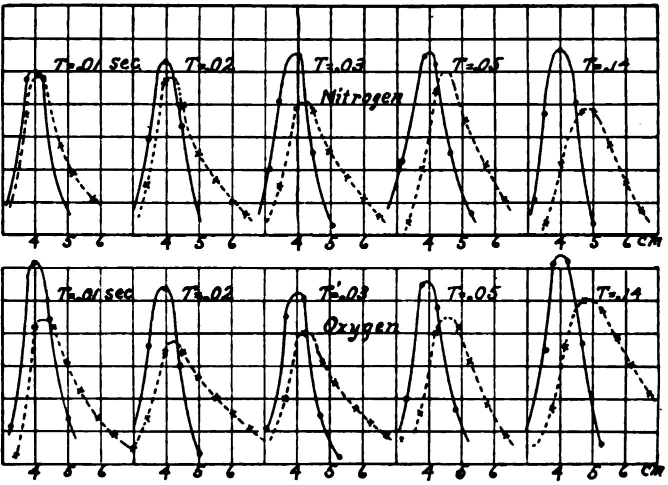

Fig. 6.

In the process of ionization of air one of the atoms of the nitrogen or oxygen molecules is caused to eject an electron, the molecule otherwise remaining intact. The electron remains free on the average a very small fraction of a second especially in the presence of oxygen. It soon attaches itself to a neutral molecule and this combination forms the negative ion. The positive remainder of the molecule which ejected the electron constitutes the initial positive ion. As the two above ions have the same mass and charge their mobilities are equal. The initial positive ion, however, soon attaches itself to a neutral molecule forming the permanent positive ion. Since its mass is twice as great as the initial positive ion or the negative ion, it has a smaller mobility.

Evidence in Support of Hypothesis.—It is of interest to consider the above hypothesis in connection with the small ion theory proposed and developed by Wellisch.[1] In this theory it was shown that the collision distance σ existing between two uncharged molecules, changes to

$$\sigma[1 + 2R/mv^2]^{1/2}$$

when one of the molecules is charged. R denotes the potential due to the polarization of the neutral molecule by the charge on the ion, and its value is shown to be

$$R = \frac{2(K - 1)e^2}{\pi n(S + S^1)^4},$$

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[1] Phil. Trans. A, Vol. 209, p. 249.

where S and S^1 are the diameters of the force spheres of the molecule and ion respectively, K is the specific inductive capacity, and e the charge.

The collision distance thus becomes

$$\sigma\left[1 + \frac{4(K - 1)e^2}{\pi n m v^2 (S + S)^4}\right]^{1/2}.$$

The expression for the reciprocal of the mean free path is

$$L^{-1} = \pi n\left[1 + \frac{M}{m}\right]^{1/2}\sigma^2.$$

This when the new expression for σ is introduced becomes

$$L^{-1} = \pi n\left(1 + \frac{M}{n}\right)^{1/2}\sigma^2\left[1 + \frac{4(K - 1)e^2}{\pi n m v^2 (S + S^1)^4}\right].$$

Substituting this in Langevin's expression for the mobility, namely

$$k = \frac{eL}{MV}$$

gives on the basis of equipartition of energy

$$k = \frac{A\eta}{\rho p}4\sqrt{2}\left(\frac{m}{M}\right)^{1/2}\left(1 + \frac{M}{m}\right)^{-1/2}\left(1 + \frac{S^1}{S}\right)^{-2}\left[1 + \frac{4(K - 1)e^2}{\pi n m v^2 (S + S^1)^4}\right]^{-1},$$

where M = the mass of the ion,
m = the mass of the molecule,
S^1 = diameter of force sphere of ion,
S = diameter of force sphere of molecule.

The ratio of two mobilities becomes:

$$\frac{k_1}{k_2} = \frac{\left(\frac{m}{M_1}\right)^{1/2}\left(1 + \frac{M_1}{m}\right)^{-1/2}\left(1 + \frac{S_1}{S}\right)^{-2}\left[1 + \frac{4(K - 1)e^2}{\pi n m v^2 (S + S_1)^4}\right]^{-1}}{\left(\frac{m}{M_2}\right)^{1/2}\left(1 + \frac{M_2}{m}\right)^{-1/2}\left(1 + \frac{S_2}{S}\right)^{-2}\left[1 + \frac{4(K - 1)e^2}{\pi n m v^2 (S + S_2)^4}\right]^{-1}}.$$

Using Wellisch's values of

$$3.70 \text{ for } \frac{(K - 1)e^2}{4\pi n m v^2 S^4}$$

and placing $S' = aS$ and $M = bm$, the above ratio becomes

$$\frac{k_1}{k_2} = \frac{\sqrt{b_2}\sqrt{1 + b_2}\,(1 + a_2)^2\left[1 + \frac{59.2}{(1 + a)^4}\right]}{\sqrt{b_1}\sqrt{1 + b_1}\,(1 + a_1)^2\left[1 + \frac{59.2}{(1 + a)^4}\right]}.$$

Let k_1 = mobility of ion of mass m, *i.e.*, $M_1 = m$, $S_1 = S$; then $a_1 = 1$, $b_1 = 1$ and

$$\frac{k_1}{k_2} = \frac{\sqrt{b_2}\sqrt{1 + b_2}(1 + a_2)^2\left[1 + \frac{59.2}{(1 + a_2)^4}\right]}{26.6}.$$

The above expression may be written

$$\frac{k_1}{k_2} = \frac{\sqrt{b_2}\sqrt{1 + b_2}\,J}{26.6},$$

where J is a function of a_2. The function J is a minimum for

$$a_2 = 1.77.$$

Using this value of a_2 in J, for the ion of mass $M_2 = 2m$, *i.e.*, $b = 2$, gives for the ratio

$$\frac{k_1}{k_2} = 1.418.$$

It is thus seen that the initial ion of $M_2 = m$ and final ion of $M = 2m$ of the hypothesis gives a mobility ratio of 1.418 when the diameter of the force sphere of the final ion is 1.77 times that of the molecule m. This is in satisfactory agreement with the observed ratio 1.40.

It is necessary to determine if other values of b and a will give the observed ratio 1.40.

Since J is a minimum for $a = 1.77$ it is evident that values of M_2 greater than $2m$ will give ratios which for all values of a_2 will be too large. For values of the mass of the ion less than $2m$, only two cases are possible namely, $M_2 = m$ and $M_2 = 3/2m$ (three atoms). For each of these there are two values of a_2 either of which will give the observed mobility ratio as may be found by substituting 1.40 for the ratio and solving for a_2. These are

$$a_2 = 0.58 \text{ and } 3.87 \text{ for } M_2 = m$$

and

$$a_2 = 0.96 \text{ and } 2.92 \text{ for } M_2 = 3/2m.$$

As the change in size is of the nature of an addition to the solid kernel, the charge remaining the same, the above values are quite untenable. The observed ratio is therefore obtained only in the case of an ion two molecules in size.

Since $\sqrt{2m/m} = \sqrt{2} = 1.414$, is in fair agreement with the observed ratio of the mobilities, the above suggests that in any one gas the mobility is approximately proportional to the inverse square root of the mass of the ion.

The velocity in the direction of the field X, obtained by an ion in the time t, is

$$v = \frac{Xe}{M}t,$$

where t is the mean free time between collisions. The average velocity of drift will therefore be

$$\bar{v} = \frac{Xe}{2M}t$$

and the mobility, which is the coefficient of X, is

$$k = \frac{e}{2M}t.$$

The value of t is determined by the velocity of temperature agitation and the velocity, which is superimposed, due to the field. As the former is large compared to the latter, t may be regarded as entirely determined by the velocity of temperature agitation V. We may consequently write

$$t = \frac{\lambda}{V},$$

where λ is the mean free path of the ion.

The mobility then is

$$k = \frac{e\lambda}{2MV}.$$

Substituting, on the basis of equipartition of energy, the value of V obtained from the relation

$$1/2MV^2 = 3/2RT$$

gives the mobility

$$k = \frac{e\lambda}{2\sqrt{M}\sqrt{3RT}}.$$

The ratio for two sets of ions then becomes

$$\frac{k_1}{k_2} = \frac{\sqrt{M_2}\lambda_1}{\sqrt{M_1}\lambda_2}.$$

The statement that the ratio of the mobilities of two ions in any one gas is proportional to the inverse ratio of the square root of their masses, therefore requires that their mean free paths be the same. This would be the case if the mean free path is determined primarily by the charge.

The indication of all the above is that the final positive ion has a mass which is twice the mass of the initial positive ion.

The question then becomes: Is one justified in assuming that the initial positive ion is one molecule in size? It is evident that this question must be answered through a knowledge of the ionization process.

The strongest evidence at the present time is the existence of free electrons at the instant of ionization. The results obtained by Franck, Haines, Wellisch, Loeb and others are conclusive on this point. On the strength of this we would conclude that the ionization process consists in the ejection of an electron. The next obvious step is to assume that the electron attaches itself to a neutral molecule rather than an atom. The chance of the first must be very much greater than the second. If this takes place then the negative ion is one molecule in size. If it is larger than one molecule the early transition stages should be detectible experimentally. Different transition stages have not been observed in these experiments.

If the negative ion is one molecule in size then the initial positive ion must be one molecule in size, since their mobilities are the same.

As shown above the indications are that the final positive ion is two molecules in size. If it is larger than this the transition stages should be detectible experimentally. This in connection with the ion in question is not observed in this investigation.

It is of interest to note that on the basis of the above, the mobilities 1.32, 1.53, 1.87, 2.64 may be predicted corresponding respectively to the ions of masses, two molecules, three atoms, one molecule, one atom.

There has just come to my hands a paper by Nolan and Harris[1] in which results are given which are interpreted as indicating the presence of several mobilities. Among these for the positive as determined by a blast method are

$$(2.5),\ 2.04,\ \ 1.79\ \ 1.52\ \ 1.37.$$

Evidence of 2.5 was only obtained by an A.C. method. Of these five values four are predicted by the above.

I am glad to take this opportunity of expressing my indebtedness to Professor W. F. G. Swann and to Professor John T. Tate for their helpful suggestions and kind interest.

PHYSICAL LABORATORY,
UNIVERSITY OF MINNESOTA,
March 9, 1922.

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[1] Proc. Roy. Irish Acad., XXXVI., A, 2, p. 31.

PHENOMENA IN GASES EXCITED BY RADIO FREQUENCY CURRENTS.

By E. O. Hulburt.

Synopsis.

Undamped Radio Frequency Vacuum Discharges through Hydrogen, Oxygen and Air.—(1) ***The spectra***, 5000–3500 Å., were found to be the same for frequencies of 3×10^5 to 4×10^6 as for 60 cycles, with currents of the same strength. (2) ***The minimum discharge potentials*** for electrode distances from 5 to 30 mm. and pressures of from 1 to 5 mm. of mercury were also found to be independent of the frequency and the same as for direct currents. A theoretical discussion of this result leads to the conclusion that the discharge is initiated by collisions of electrons, rather than of gaseous ions, with gas molecules. (3) ***Persistence*** of each discharge was studied with the aid of a mirror rotating 200 times per second. Damped discharges with a frequency of 10^6 cycles or less showed separate flashes but those with higher frequencies were blended together. This difference may perhaps be due to the limitations of the apparatus used. With damped oscillations the color of the discharge changed with the voltage as would be expected.

Introductory.

LITTLE is known of the behavior of gases stimulated into luminosity by alternating electric currents of radio frequency and the present investigation was undertaken for the purpose of obtaining information on this subject. By radio frequency we mean the range of frequencies usually employed in the radio art, *i.e.*, the range between 10^5 and 10^7 alternations per second. The description of the work is taken up in three parts as follows, the radio frequency spectra, the potentials necessary to set up luminosity, and the radio frequency flashes of light.

The Radio Frequency Spectra.

Numerous experiments on electrically excited gases have been performed concerning the relations between the type of electrical excitation and the spectrum of the luminous gas and in some cases[1] potentials alternating at radio frequencies have been used. Recently Dunoyer[2] has discovered new spectra from certain metallic vapors by the use of damped radio frequency currents. None of these experiments, however, tell definitely the effect, if any, on the spectrum of the gas occasioned by the frequency of the alternating current. The advent of the oscillating electron-tube methods of generating radio frequency currents has rendered possible a direct answer to this question and the present work has been undertaken with this in view. It may be stated in advance that for the cases here investigated the spectrum of the gas remained unchanged when the frequency was increased from sixty to a million or more cycles per second, other factors being kept constant.

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[1] Wiedemann and Ebert, Wied. Ann., 50, 221, 1893; Himstedt, Wied. Ann., 52, 473, 1894.

[2] Comptes Rendus, 173, 350, 1921; 173, 472, 1921.

An electron-tube oscillating circuit was arranged for the production of currents of frequencies from 0.43×10^7 to 10^5 cycles per second, *i.e.*, wave-lengths from 70 to 3,000 meters. The tube was a fifty watt power tube with 1,000 volts on the plate and a filament current of 6.5 amperes. By means of this generating circuit radio frequency current could be induced in coil *b*, Fig. 1, which was in series with a variable air condenser *c* and a hot wire ammeter *a*. By means of a switch *s* the end-on discharge tube *d*, which was in series with the thermogalvanometer *t*, could be connected either across *c* or to the high potential terminals of a ½ kw., 25,000 volt transformer *p* actuated by 60-cycle current. The discharge tube was of glass with aluminum electrodes arranged out of line with the capillary. The capillary was 10 cm. long and with an internal diameter of 5 mm. Hydrogen, oxygen, and air, purified by sodium hydroxide solution, sulphuric acid and phosporous pentoxide, at a pressure of 3 mm. or less were used in the tube. The generating circuit and the circuit *bc* were tuned to the desired frequency. With 4 amperes through *a* and with *c* adjusted to, say, 500 $\mu\mu F$, the discharge tube glowed brilliantly. The increase in the current through the tube when luminosity occurred was about one half of a milliampere. When the 60-cycle transformer was used the current through *t* was adjusted to be one half of a milliampere.

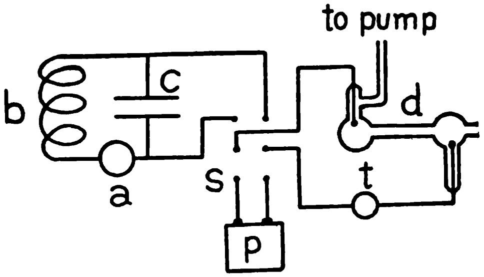

Fig. 1.

The spectra were photographed throughout the region from 5000 A to 3500 A in the first order of a concave grating of two meters radius of curvature ruled 14435 lines to the inch. The spectra of hydrogen, oxygen and air excited by currents of frequencies 60, 3×10^5, 10^6 and 0.43×10^7 were recorded, and in all cases the spectrum was found to be unmodified by the change in frequency. With hydrogen about three hundred lines of the secondary spectrum and a faint continuous background appeared on the plates. The Balmer lines were faint. Oxygen exhibited the fine-lined band spectrum. Air showed the oxygen and nitrogen lines.

THE POTENTIAL NECESSARY TO SET UP LUMINOSITY.

Measurements of the potentials just sufficient to set up luminosity in a gas for radio frequency and direct currents yielded information concerning the cause of the luminosity. For this purpose a bulb was equipped with disc electrodes 1.5 cm. in diameter whose distance apart could be varied. The potential difference of the electrodes was measured by an electrostatic voltmeter. The maximum reading of the instrument was 1,000 volts and above 200 volts the indications were accurate within 10 volts. To make a measurement the potential difference of the electrodes was increased very slowly and the voltage observed when the bulb suddenly burst into luminosity. Table I. shows a series of readings for hydrogen when the electrodes were 14 mm. apart. In the table the numbers for the alternating voltages were the maximum values of the voltages, and were obtained by multiplying the electrometer readings by $\sqrt{2}$. The conclusion from Table I. and from similar tables for hydrogen and oxygen, for electrode distances from 5 to 30 mm. and for pressures from 1 to 5 mm. of mercury, was that for a specified electrode distance and gas pressure the voltage just sufficient to produce luminosity did not change when the frequency was varied over a wide range.

TABLE I.

Pressure in Mm. of Hg.	Frequency.			
	0	60	0.86×10^6	5.3×10^6
3.4	640 volts	635	652	642
2.0	430	436	436	424
0.9	410	424	404	409

We turn to a consideration of the electron theory in this connection. It is known that luminosity is set up when collision occurs between a molecule of the gas and an electron or ion which has acquired a certain critical velocity. A molecule or atom may acquire sufficient energy to become luminous not only by a single violent encounter but also by the accumulation of energy from a succession of milder encounters. It is reasonable to suppose that the luminosity is *begun* by a single violent encounter, for this process is conceivably much quicker than the other. We proceed to find an expression for the critical velocity of the ion partaking in the violent encounter in the case of a steady electric field and of an alternating electric field.

We assume a Lorentz contractile electron of charge e and mass m for small velocities. The electron moves from rest under the influence of a homogeneous steady electric field E which is in the direction of the X axis. The effects on the motion due to radiation from the accelerated electron are neglected. If c.g.s. electromagnetic units are used the equation of motion of the electron is in Newtonian notation

$$x = E\frac{e}{m}\left(1 - \frac{\dot{x}^2}{c_2}\right)^{3/2}, \tag{1}$$

where x is the positional coördinate of the electron, and c is the velocity of light *in vacuo*. With initial conditions $t = x = \dot{x} = 0$, the solution of (1) is found to be

$$x = \frac{ct}{\sqrt{\frac{c^2m^2}{E^2e^2} + t^2}} \tag{2}$$

and

$$x = c\sqrt{\frac{c^2m^2}{E^2e^2} + t^2} - \frac{c^2m}{Ee}. \tag{3}$$

Eliminating the time t between (2) and (3) gives

$$\dot{x} = \frac{\sqrt{\frac{x^2}{c^2} + \frac{2xm}{Ee}}}{\frac{x}{c^2} + \frac{m}{Ee}}. \tag{4}$$

Suppose the electron to move in an alternating electric field of amplitude E_1, and frequency $\omega/2\pi$. The effects upon the motion due to radiation from the field and the electron are neglected. Letting the subscript 1 denote the alternating potential case, the equation of motion of the electron is

$$\ddot{x}_1 = E_1\frac{e}{m}\left(1 - \frac{\dot{x}_1^2}{c^2}\right)^{3/2} \cos \omega t. \tag{5}$$

With initial conditions $t = x_1 = \dot{x}_1 = 0$, the solution of (5) is

$$\dot{x}_1 = \frac{\frac{E_1ec}{m\omega} \sin \omega t}{\sqrt{c^2 + \frac{E_1^2e^2}{m^2\omega^2} \sin^2 \omega t}} \tag{6}$$

and

$$x = \frac{c}{\omega}\left[\cos^{-1}(\alpha\cos\omega t) - \cos^{-1}\alpha\right], \tag{7}$$

where

$$\alpha = \frac{\dfrac{E_1 e}{m}}{\sqrt{\dfrac{E_1^2e^2}{m^2} + \omega^2c^2}}. \tag{8}$$

Eliminating t between (6) and (7) gives

$$\dot{x}_1 = c\,\frac{\sqrt{\alpha^2 - \cos^2\left(\dfrac{\omega x_1}{c} + \cos^{-1}\alpha\right)}}{\sin\left(\dfrac{\omega x_1}{c} + \cos^{-1}\alpha\right)}. \tag{9}$$

When E and E_1 are the potentials just sufficient to set up luminosity we may equate (4) and (9).

This leads to

$$\frac{\sqrt{\dfrac{x^2}{c^2} + \dfrac{2xm}{Ee}}}{\dfrac{x}{c^2} + \dfrac{m}{Ee}} = c\,\frac{\sqrt{\alpha^2 - \cos^2\left(\dfrac{\omega x_1}{c} + \cos^{-1}\alpha\right)}}{\sin\left(\dfrac{\omega x_1}{c} + \cos^{-1}\alpha\right)}. \tag{10}$$

Where α is given by (8), and x and x_1 are now the distances the electron travels before it attains the critical velocity for the direct and alternating potential cases, respectively. When $\omega = 0$ (10) becomes an identity. Further, if e/m refers to the charged atom or molecule and not to the electron, the variation of mass with velocity may be neglected, and (10) simplifies to

$$E_1x_1 - Ex = \frac{x_1^2\omega^2m}{2e}. \tag{11}$$

We now make use of the experimental fact that within the error of experiment E was equal to E_1 for all the cases examined. The following numerical values were chosen: $e/m = 1.77 \times 10^7$ for the electron, $\omega = 10^7$, $x = x_1 = 1$, and $c = 3 \times 10^{10}$. x and x_1 were unknown, but since they could not be greater than the distance between the electrodes we have taken them to be of the order of one centimeter. Their exact values are of little importance in the calculations from (10). When these values are substituted in (10) it is found that E_1 is greater than E by a quantity of the order of magnitude of one thousandth part of a volt, and that not until ωx_1 becomes as large as c does $E\delta$ differ appreciably from

E_1. This is in accord with the experimental results. If we chose the value of e/m for the hydrogen molecule, *i.e.*, 0.5×10^4, $\omega = 10^7$, $x = x_1 = 1$, and $c = 3 \times 10^{10}$, upon substitution in (11) we find $E_1 - E = 100$ volts and for the oxygen molecule $E_1 - E = 1600$ volts. Of course it is not permissible to use $x = x_1$ in (11), but since x_1 must always be greater than x the values of $E_1 - E$ just given are minimum values. Further it is seen from (11) that $E_1x_1 - Ex$ increases with ω^2. These results are clearly at variance with the experimental results. We therefore conclude that the charged particle which collides with the gaseous molecule, thereby originating the luminosity in the gas, is the electron. After luminosity has once set in subsequent ionization is caused by both electrons and charged molecules or atoms as J. J. Thomson and others have shown.

THE RADIO FREQUENCY FLASHES.

In order to determine whether the luminosity of a gas stimulated by radio frequency current flickered at a radio frequency the discharge tube *d*, Fig. 2, excited by damped-wave radio frequency current was pointed at a mirror *m*, 3 cms. square, about four meters distant, which rotated 12,000 times per minute. The light reflected from the mirror was observed in a low-power telescope *h*. Fig. 2 shows the arrangement. The 25,000 volt transformer *p* charged the condenser *c* which discharged through the coil *b*, the tube *d*, the hot-wire ammeter *a*, and the spark gap *g*. When the mirror was rotated the flashes from the tube were seen spread out into streaks of light. Each streak consisted of a series of separate flashes occurring at the frequency of the radio frequency current through the gas. The general appearance is sketched in Fig. 3. Observations on hydrogen, oxygen, air, and argon showed that the radio frequency striations were discernable for frequencies as high as 10^6, but for frequencies greater than this the streak appeared continuous. The shortness of the time of a dark striation is worthy of remark. For example, in the case of hydrogen at 3 mm. pressure a frequency of $0.86 \times$

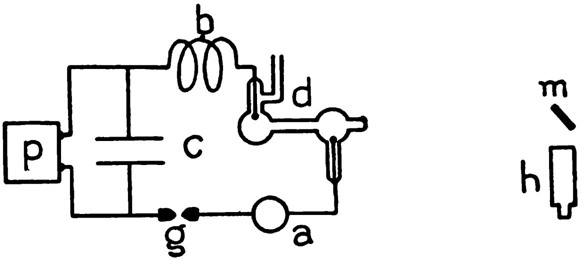

Fig. 2.

10^6 produced dark striations whose length and intensity were perhaps one tenth of the length and intensity of a bright striation. Thus in 6×10^{-8} seconds the intensity of the gas passed from a high value to a low one and back to a high value again. The fact that there was an upper limit of frequency above which no striations could be seen was due in part to the limitations of the apparatus, and in part to the greater damping of the oscillations at the higher frequencies as shown by the shortness of the streak and the logarithmic decrement of the circuit. The non-appearance of the dark striations may also have been caused by the persistence of the luminosity, for W. Wien[1] and G. Mie[2] have shown in the case of the light from canal rays of hydrogen and oxygen that the time for the luminosity to decrease to $1/\epsilon\delta$th of its value was of the order of 10^{-8} seconds.

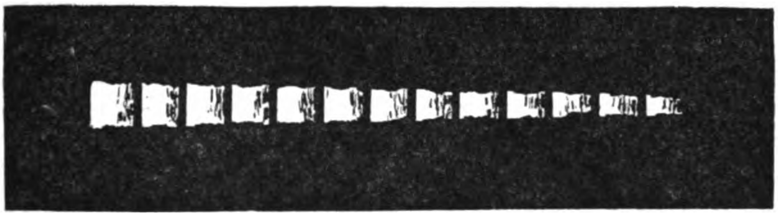

Fig. 3.

With hydrogen or argon in the discharge tube the first one or two flashes of a radio frequency series, such as pictured in Fig. 3, were nearly white, the next few flashes pink, and the last flashes red. The cause of this was attributed to the energy distribution in the visible spectrum of the gas. In the case of hydrogen the condenser discharge brought out the Balmer lines strongly with the secondary spectrum relatively weak. The first few flashes owed their whiter color to the predominance of H_β and H_γ caused by the relatively great intensity of the first few oscillatory discharges of the condenser. As the discharges become less violent H_α became more prominent and colored the later flashes red.

State University of Iowa,
March, 1922.

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[1] Ann. d. Phys., 66, 229, 1921.

[2] Ann. d. Phys., 66, 237, 1921.

THE EFFECT OF THE MAGNETIC FIELD ON THE ABSORPTION OF X-RAYS.

14 pages

By Joseph A. Becker.

Synopsis.

Effect of a magnetic field on the absorption of x-rays, if it can be measured, would have an important bearing on the theory of atomic structure. Since the effect is very small, a differential method was adopted and by eliminating various spurious effects the apparatus was made sensitive enough to detect a change of 1 part in 10,000. Observations were made with a peak voltage of 80 kv. across the Coolidge tube (mean wave-length about 0.3 Å.) and with a magnetic field H of about 18,000 gauss. For H perpendicular to the rays, *aluminum, carbon, copper, iron, nickel, platinum, zinc, and silver* showed changes in absorption coefficients of $+8 \pm 6$, -5.6 ± 2, $+0.8 \pm 0.4$, -10 ± 2, $+1.6 \pm 0.5$, $+1.7 \pm 0.4$, -1.2 ± 0.4 and $+1.6 \pm 0.8$ parts in 10,000 respectively, while with H parallel to the rays the corresponding changes were $+2.7 \pm 1$, $+3 \pm 1$, $+1.4 \pm 1$, -0.5 ± 2, $+0.7 \pm 2$, $+1.1 \pm 1$ and $+1.3 \pm 1 \times 10^{-4}$, silver not being tried. These results are in accord with the hypothesis that the magnetic properties are largely determined by the outer shell or valency electrons, since at the wave-lengths used by far the greater part of the absorption is due to the inner electrons. Wood was also tested with softer rays having a mean wave-length of about 1.2 Å., and showed a change of $+80 \pm 20 \times 10^{-4}$ as compared with 3×10^{-4} for carbon for wave-length 0.3 Å. Following the suggestion of this result it is proposed to do further work with light elements and softer x-rays.

Differential Method of Measuring Small Changes of Intensity of an X-ray Beam.—The apparatus, which includes two similar ionization chambers connected so that the ionization currents nearly neutralize each other, is described in detail together with the precautions necessary to eliminate various sources of error and to attain the sensitivity mentioned above.

Bumstead Electroscope.—A simple type is described. Care should be taken to eliminate convection currents within the instrument.

THE following investigation was undertaken because of the conviction that the structure of the atom cannot be satisfactorily explained without taking into account magnetic forces. It was hoped that an applied magnetic field would orient the ultimate magnetic particle and that this shifting would result in a measurable change in the absorption of x-rays. A study of this effect would throw a new light on the nature of the ultimate magnetic particle and on its function in the atom.

This search is not new. In 1914 and 1916 Dr. Forman[1] sought for this effect in iron. In his second paper he reports an increase in absorption of five to seven parts in a thousand when iron is magnetized in a direction parallel to the x-ray beam. Soon thereafter A. H. Compton[2] developed his theory of scattering and later stated "that the effect observed by Forman is of the order of magnitude to be expected if the electrons are rings of electricity which are oriented by the magnetic field."[1] This led him to look for a change in γ-ray absorption in magnetized and unmagnetized iron. He reports negative results of .023 ± .018 and .004 ± .019.[3]

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[1] Phys. Rev., *3*, 306–313, 1914 and *7*, 119–124, 1916.

[2] J. Wash. Acad. Sci. *8*, 1, 1918 and Phys. Rev., *14*, 20–43 and 247–259, 1919.

Since 1916 our knowledge of x-ray production and absorption, as well as the technique of control and measurement, has advanced sufficiently to warrant a repetition of Forman's work as well as an extension to other materials than iron.

Apparatus.

The method used is essentially a differential one and is necessarily so because the changes sought are small.

The general arrangement of apparatus was much the same as that used by Forman. A radiation-type, tungsten-target Coolidge tube, *T*,[2] is practically completely enclosed in a lead box *L*, Fig. 1, and sends two beams of x-rays through three pairs of preliminary lead slits, through the absorbers *A* and *A′*, and into two identical ionization chambers I_1 and I_2. The rods R_1 and R_2 are connected together and to the leaf of a Bumstead electroscope *E*.[3] This system can be earthed by means of a mercury-break key, and is shielded from electrostatic disturbances by a tin shield *Sh*. The casings of the ionization chambers, as well as the movable plates of the electroscope, are connected to the terminals of a 420-volt battery of dry cells, *B*, whose middle point is earthed. *G* is a

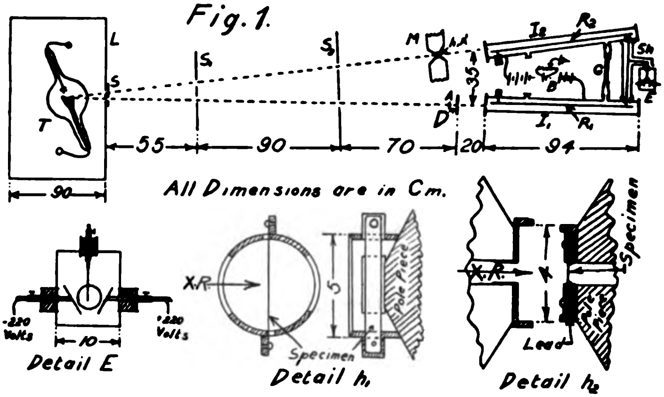

Fig. 1.

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[1] Phys. Rev., *17*, 38–41, 1921.

[2] Very kindly placed at the disposal of Prof. Richtmyer by Dr. Coolidge.

[3] Am. J. of Sci., *32*, 405–406, 1911 and Phil. Mag., *22*, 910, 1911.

glass tube connecting the two chambers. M is a powerful electromagnet of Swiss type. The diameter of the face of the pole-pieces was 2 cm. in the first part of the investigation and 4 cm. in the second part. h is a holder to be described in detail later. D is a rectangular opening of lead, the upper edge of which is attached to a slow motion screw.

The procedure is as follows: one specimen is placed between the pole-pieces, while an exactly similar one is placed in front of D. The size of the slit at D is varied until practically no net charge accumulates on the rods R_1R_2 and the leaf shows either a small rate of drift or none at all. The magnet is energized. If the absorption of the specimen in the field is increased, the ionization in I_2 will decrease, and the leaf will show a change in the rate of drift ($\Delta\delta$) where δ is the rate of drift in divisions per minute. By subsequently determining how much the height of the slit at D must be increased to produce the same $\Delta\delta$ we can compute $\Delta I/I$, the proportional change in the intensity of the transmitted beam. Then by means of a formula to be developed later we can compute $\Delta\mu/\mu$, the proportional change in the absorption coefficient due to the field H.

Since the effect is small it is necessary to be able to keep the two ionization currents balanced to within 1 or 2 parts in 10,000. Consequently every effort was made to reduce the errors to a minimum. The larger part of the time was taken up in determining and eliminating spurious changes in δ. The following list gives the chief factors to be guarded against.

SOURCES OF ERROR.

(*a*) Electrostatic effects.
(*b*) Unsteadiness of leaf of electroscope.
(*c*) High-resistance leaks.
(*d*) Stray x-radiation.
(*e*) Slight changes in the position of the focal spot.
(*f*) Changes of current through the tube.
(*g*) Peculiarities of the ionization chambers.
(*h*) Effect of the magnetic field on the tube or ionization chambers.
(*i*) Movement of the specimen caused by H or by the slight shifting of the pole-pieces.

To show how these errors were eliminated it is necessary to give a detailed description of the apparatus.

THE ELECTROSCOPE.

Fig. 1 shows a detail drawing of the electroscope. It can be constructed by an amateur mechanic in a short time. The brass box was made detachable, but the joints were sealed with wax to make them air tight. The plates and the leaf are adjustable. Sulphur insulation was found convenient and satisfactory. The position of a definite point on the gold-leaf was observed through a low-power microscope with a 50-division scale in the ocular. These 50 divisions correspond to approximately 2 mm. At first considerable difficulty was encountered in keeping the grounded leaf at rest. The trouble was finally ascribed to heat convection currents, and was eliminated by completely enclosing the instrument with a cardboard housing. The working sensitivity of the leaf was about 80 div. per volt on the leaf. This sensitivity could easily have been increased four or five fold by either lowering the leaf, moving both plates closer, or by increasing the voltage on the plates.[1] At the high sensitivities it becomes somewhat more difficult to keep the position of the leaf steady. Unsymmetrical changes of voltage on the plates were about one fifth as effective in deflecting the leaf as the same voltage on the leaf, *e.g.*, if the ground is shifted one volt the resultant deflection is the same as if the leaf had been charged to .2 volt. This fact necessitated keeping the relative voltages on the plates constant to within 10 millivolts. When not too old, the dry cells proved satisfactory so long as their temperature was kept constant.

The drift in the leaf due to change of plate voltage, high resistance leaks, and electrostatic disturbances was seldom more than 5 divisions in half an hour. Neither was the rate of drift increased by running the x-ray tube with the openings at h and D closed by small lead plates. This shows that the first four sources of error mentioned above were effectively eliminated. To accomplish this it was found essential completely to inclose the tube with lead and put up the preliminary screens.

Sources of error e, f, and g were found by repeatedly observing that δ would change radically whenever the current through the tube changed. At this time the high tension for the tube was furnished by a G. E. x-ray transformer while the filament was supplied from a step-down transformer. Even though the primary of both transformers was supplied from a rotary converter (D.C. to A.C.) whose voltage could be kept constant to within 2 per cent., yet the current through the tube would vary as much as 50 per cent. Ideally this should not have disturbed a balance since both beams should be affected equally. Practically it did and the only satisfactory way of keeping the current steady was to light the filament by means of a 12-volt storage battery in the high-tension circuit. The filament current was varied by means of a slide-resistance operated by an insulated handle. Even with this arrangement the contacts in the filament circuit were gone over periodically to insure steady currents.

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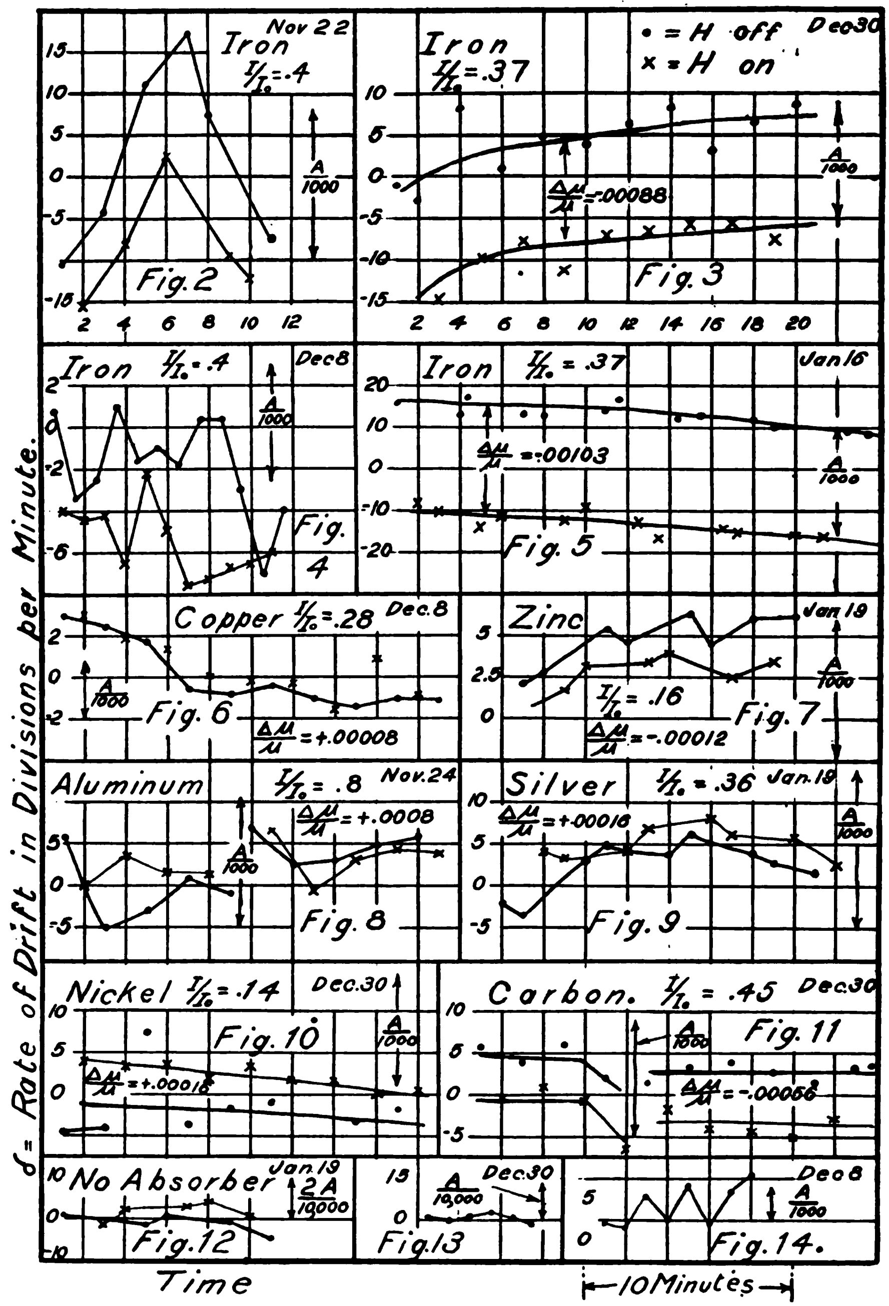
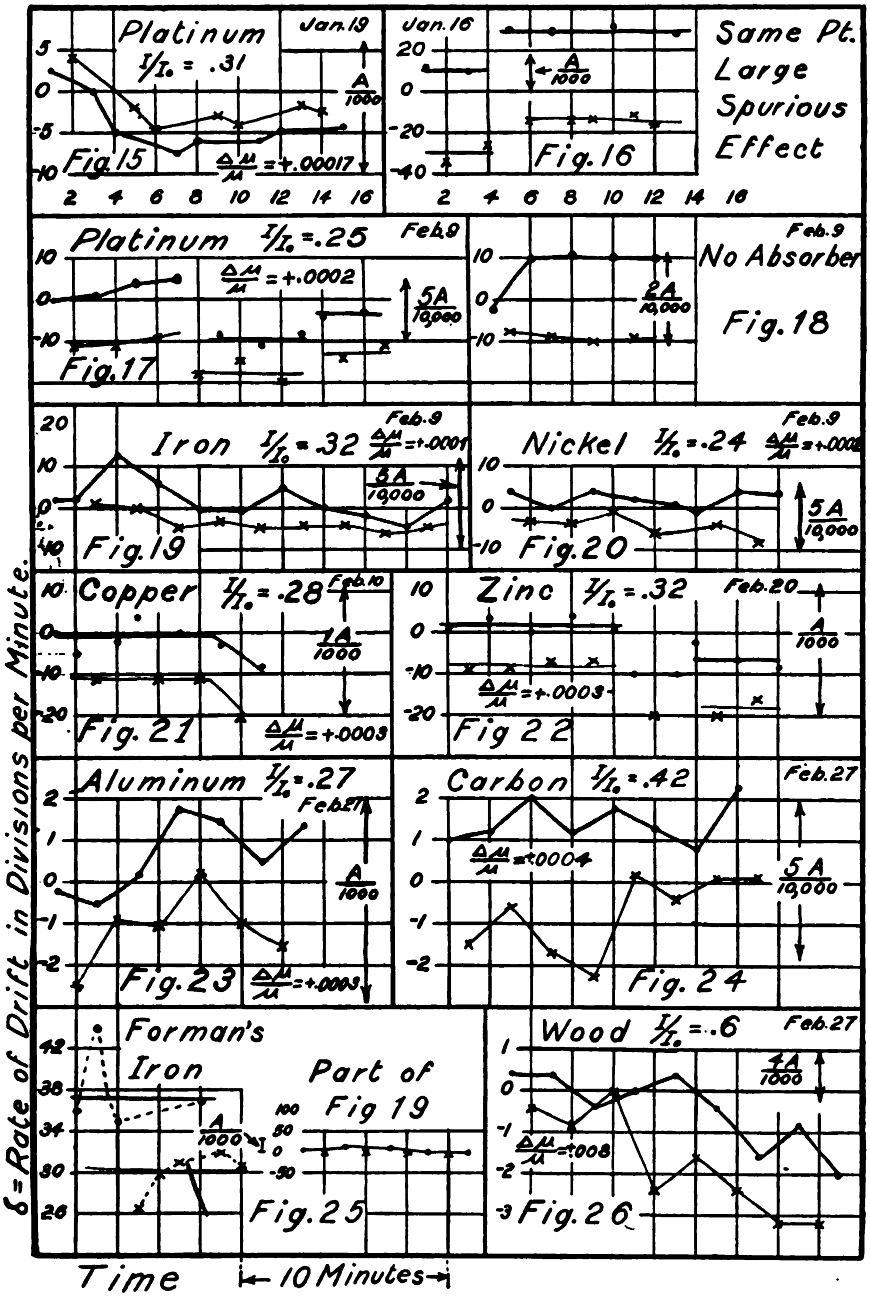
[1] Dadourian, Phys. Rev., 14, 238, 1919, obtained a working sensitivity of 5,000 divisions per volt.



In all Figs. the values of δ for H off are represented by $\cdot$; for H on, by an x. H = approx. 18,000 gauss.

In Figs. 2 to 16, H was perpendicular to the x-rays; the voltage was 80 kv. peak; a $+\Delta\delta$ means a decrease in I, or an increase in μ.



In Figs. 17 to 24, H was parallel to X; the voltage was 80 kv. peak; a $+\Delta\delta$ means an increase in I or a decrease in μ.

In Fig. 26, H was parallel to X; the voltage was 27 kv. peak; a $+\Delta\delta$ means a decrease in μ.

A pin-hole picture of the focal spot showed that it consisted of a ring 7/16 inch in diameter with two irregular small areas inside. Consequently if the first slit S is narrow and the focal spot for any reason shifts, even though the shift is so slight as to be imperceptible, a slightly different area becomes effective in illuminating the slit at D and thus the balance is destroyed. The preliminary slits were therefore made 3/4 inch wide while the final slits at D and h were only 1/8 to 1/4 inch wide. In this way every point of the final slit received radiation from every point of the focal spot even though the focal spot did shift slightly. Incidentally, widening the preliminary slits also increased the available energy. The improvement brought about by this change shows up clearly by contrasting the steadiness in Figs. 2 and 14 for narrow slits with Figs. 3 and 13 for the widened slits.

The ionization chambers were made of brass tubing and were fitted with square ends. They were mounted on sulphur supports. The rods were supported and insulated by sulphur plugs containing the usual earthed guard rings. The chambers were filled with methyl bromide. Unfortunately this gas in the presence of moisture reacts with zinc and copper thus making it necessary to refill the chambers every three or four weeks. When doing so, care was taken to fill both chambers to the same pressure, otherwise a change in the tube current of .1 milliamp might unbalance the ionization in the chambers by several parts in 1,000. Later the two chambers were connected by a glass tube.

During the course of the investigation it was noticed that the balance was particularly sensitive to slight shifts in the rear end of the ionization chambers. A further study revealed the fact that an appreciable percentage of the ionization was caused by photoelectrons emitted by the rear end of the chamber. Materials of low atomic weight were found to cause a smaller increase in the ionization than those of high atomic weight. The arrangement decided upon as least troublesome was an aluminum plate coated on the inside with wax.

SPURIOUS EFFECTS DUE TO THE MAGNETIC FIELD H.

Forman found that the stray field of his electromagnet deflected the electron stream in his tube. He finally remedied the difficulty by means of compensating coils and iron screens. The magnet in this present investigation was placed at a considerable distance from the tube. Its stray field near the tube was less than the earth's field and when possible was opposed to it. The final test as to whether the stray magnetic field affects either the tube or the ionization is to make blank runs either with no absorbers or with absorbers in front of the magnet. Several such runs were made and in no case was any effect greater than 2 parts in 10,000 obtained. (See Fig. 18).

Several times large apparent changes in absorption were noted when the specimen was between the pole-pieces, but in all such cases it could be shown that either the field distorted the specimen or the shifting of the pole-pieces displaced the specimen. This was particularly true in the case of iron and nickel, and with thin specimens. Fig. 16 shows a spurious change of about 2½ parts in 1,000. Due to the high absorption coefficient for platinum the specimen was only 1 or 2 mils thick. Small forces might easily distort the thin specimen. When this same specimen was pasted on a thin uniform strip of wood and another run taken, as shown in Fig. 15, ΔI is only a few parts in 10,000. Practically the same result was obtained when the specimen was tightly clamped in the holder.

THE SPECIMEN HOLDERS.

Two holders h_1 and h_2 were designed and are shown in detail in Fig. 1. h_1, which was used when H was perpendicular to the rays, consists of a brass collar with bevelled edges which match the pole-pieces. Two screws fasten the specimen to two ledges at opposite ends of a diameter. Perpendicular to this diameter are openings to allow the beam to pass. This holder may not be as reliable as the accuracy of the remainder of the outfit warrants. Consequently a new one has been designed which, it is hoped, will give more reliable results.

Holder h_2 was carefully designed and constructed. It was used when H was parallel to the rays. The specimen is firmly held in front of the lead opening by means of screws passing through the brass cover. The pole-pieces are firmly screwed up against the holder.

THE FINAL SLIT AT D.

The opening at D was usually 3/16 inch wide and about 1/2 inch high. A balance was obtained by changing the height by means of the micrometer screw. One turn corresponds to 1/100 inch and there are 100 divisions on the drum. Thus with a slit 1/2 inch high, 5 drum divisions ($5D$) correspond to a change in area of 1 part in 1,000, *i.e.*, $A/1{,}000$. By noting δ for a series of positions of the drum, $\Delta\delta$ for $10D$, or else $\Delta\delta$ for $A/1{,}000$ can be computed. The uniformity of intensity of the x-ray beam over the whole opening was shown by the fact that this ratio was independent of the height of the opening.

In all measurements of large rates of drift, say greater than 60 divisions per minute, it was found necessary, in order to get consistent results, to apply a correction to the observed δ. Table I. gives the values of the corrections to be added to the absolute value of the observed δ. These corrections were obtained by noting δ for a number of openings differing by equal small steps and plotting δ against the opening. Instead of a straight line, a curve was obtained which deviated more and more from the straight line as δ increased. The deviations gave the corrections to be added. This lag is probably due to air friction and is a function of the dimensions and shape of the leaf and the air pressure. It is analogous to the lag in a quadrant electrometer.

TABLE I.

Observed δ	50	100	150	200	250	300	400
Correction	.5	2.5	9	19	37	60	90

SENSITIVITY OF APPARATUS.

To show how sensitive the apparatus is, one need only obtain a balance, and then interpose a very thin sheet of paper. After a few seconds' lag the leaf begins to drift and continues to do so until a few seconds after the paper is removed. A few degrees change in temperature in the slit *D* can be detected; the slight "give" in the floors caused by a person walking past the supports for the slit *D* produces an observable effect; air currents also cause disturbances. Under these circumstances it seems almost hopeless to try to measure an effect less than one part in 1,000 with an accuracy better than 10 per cent. However, if the temperature and current could be maintained constant and if mechanical disturbances were minimized, the apparatus could detect changes as small as 2 or 3 parts in 100,000.

COURSE OF A COMPLETE RUN.

The following illustrates the course of a complete run.

Voltage across tube: 80 kv. peak.

Sensitivity of leaf: 44.2 div./volt.

1. Steady test: x-rays shut off by lead plates. Position of leaf every 15 seconds:

25.2	25.2	25.0	25.0	24.9	24.9	24.9	24.8	24.8	24.8	24.7	24.7
24.7	24.5	24.4	24.2	24.2	24.2	24.2	24.2	24.1	24.0	24.0	24.0
24.0	24.0	23.9	23.8	23.9	23.9	23.9	23.8	23.7	23.6	23.6	23.7
23.7	23.7	23.7	23.6								

2. Sensitivity determination with no absorber in.

Size of opening = 3,900 drum divisions or 3,900 *D*,

Drum scale 20 up $\delta = -40 \times 60/11.4 = -210$ Corrected $\delta = -230$,

Drum scale 25 up $\delta = -23.3 \times 60/30 = -46.6$ Corrected $\delta = -47$,

Drum scale 30 up $\delta = 40 \times 60/18.9 = 127$ Corrected $\delta = +131$,

$$\Delta\delta/10D = 180 \times 2 = 360 \text{ for } 2.2 \text{ milliamps} = 82 \text{ per milliamp},$$
$$\Delta\delta \text{ for } A/1000 = \Delta\delta/10D \times 3.9/10 = 140.$$

3. Steady test with x-rays entering chambers. Readings of leaf every 15 seconds:

19.0	19.5	18.5	19.5	20.0	20.7	19.5	18.5	19.7	21.0	22.0	21.0
21.0	21.5	21.8	22.5	24.0	23.8	24.0	25.0	25.3	25.0	24.0	24.0

4. Sensitivity with iron absorber in. Opening: $3800D$.

Drum 40 up $\delta = -40 \times 60/15 = -160$ Corrected $\delta = -170$,
Drum 60 up $\delta = -20 \times 60/13 = -92$ Corrected $\delta = -94$,
Drum 80 up $\delta = -12$ Corrected $\delta = -12$,

$$\Delta\delta/10D = (76 + 82)/2 \times 2 = 39.5 \text{ for } 1.3 \text{ milliamps} = 30.4 \text{ per milliamp},$$

$$I/I_0 = \frac{\Delta\delta/10D \text{ for Fe absorber}}{\Delta\delta/10D \text{ for no absorber}} = 30.4/82 = .37,$$
$$\Delta\delta \text{ for } A/1000 = (39.5/10) \times 3.8 = 15.$$

5. Effect of magnetic field on absorption of iron. $H = 18{,}000$ gauss. H is put on for one minute every other minute starting with the second. The position of the leaf is read every 15 seconds.

		H Off———	———	| Switch closed	———	———*H* On		Switch opened
33.0	32.8	33.0	34.0	33.0	31.5	29.2	25.5	24.5
	26.0	28.0	29.7	30.8	29.0	26.0	25.0	24.8
	26.2	30.0	31.2	34.0	32.5	30.0	28.3	28.5
	28.8	29.5	30.5	30.5	29.5	29.0	27.5	30.0
	31.0	34.0	35.8	36.5	34.0	32.0	30.0	29.0
	31.0	33.0	35.5	38.0				

A positive $\Delta\delta$ means an increase in absorption, or a decrease in I.

From this data the average δ for each minute was computed and plotted in the latter half of Fig. 3.

This figure shows a change of δ due to H equal to -13 div. Since $\Delta\delta$ for $A/1000 = 15$;

$$\frac{\Delta I}{I} = -\frac{-13}{15 \times 1000} = +\frac{8.7}{10{,}000}.$$

From a formula developed below

$$\frac{\Delta\mu}{\mu} = -\frac{1}{\log_e(I_0/I)} \cdot \frac{\Delta I}{I} = -1.005\frac{+8.7}{10{,}000} = \frac{-8.8}{10{,}000}.$$

Consequently a field of 18,000 gauss decreases the absorption coefficient of iron by 8.8 parts in 10,000.

DEVELOPMENT OF FORMULÆ.

As is well known,

$$I = I_0 e^{-\mu t}. \tag{1}$$

If μ can be made to change in a given specimen, then

$$\frac{dI}{d\mu} = -tI_0 e^{-\mu t} = \frac{\Delta I}{\Delta \mu} = -tI \tag{2}$$

or

$$\frac{\Delta I}{I} = -t\Delta\mu.$$

From (1)

$$t = \frac{\log(I_0/I)}{\mu}; \quad \therefore \frac{\Delta I}{I} = -\frac{\Delta\mu}{\mu} \times \log\left(\frac{I_0}{I}\right)$$

or

$$\frac{\Delta\mu}{\mu} = -\frac{1}{\log(I_0/I)} \cdot \frac{\Delta I}{I}. \tag{3}$$

Given: I_0, μ, and $\Delta\mu$ for a certain material. What is the best thickness to use so that ΔI shall be a maximum?

From (2)

$$\Delta I = -I_0 t e^{-\mu t}\Delta\mu$$

For a maximum

$$\frac{d(\Delta I)}{dt} = 0$$

or

$$-I_0\Delta\mu(e^{-\mu t} - \mu t e^{-\mu t}) = 0$$

Since I_0, $\Delta\mu$, and $e^{-\mu t}$ are not zero,

$$1 - \mu t = 0 \qquad \text{or} \qquad \mu t = 1$$

or

$$\log_e I_0/I = 1, \qquad I_0/I = 2.73; \qquad I/I_0 = .368.$$

That is ΔI, which determines $\Delta\delta$, will be greatest if t is so chosen that $I/I_0 = .368$.

RESULTS.

Figs. 2–16 show the results obtained with H perpendicular to the path of the x-rays; Figs. 17–26, the results for H parallel to the x-rays. For all but the last two figures the peak voltage across the tube was about 80 kilovolts, which corresponds to a minimum wave-length of .15 Å. The maximum energy was probably in the neighborhood of .3 Å. Each figure contains the date on which the data were obtained, the values of

$\Delta I/I$, $\Delta\mu/\mu$, and $\Delta\delta$ for $A/1000$. It is important to take this last-named factor into account when comparing the curves.

A comparison of the steadiness of this apparatus with that attained by Forman is given in Fig. 25 which shows Forman's results for iron with 81 kv. (R.M.S.) across the tube, and the present result for iron under similar conditions, both plotted to practically the same scale.

Figure 26 shows one of two preliminary runs with a peak voltage of 27 kv. across the tube. A previous run on wood at the higher voltage had revealed a $\Delta\mu/\mu$ of 4 or 5 parts in 10,000. At the lower voltage the sensitivity, consistency, and reliability are considerably less but still $\Delta\mu/\mu$ is clearly about 8 parts in 1,000 or about 16 times as large as before. This would indicate that larger changes may reasonably be looked for at longer wave-lengths with low atomic weight elements. This clue, it is hoped, can be followed up in the next few months.

The results show that while the magnetic field does change the absorption of x-rays in various materials the effects for wave-lengths near .3 Å. are small. At this wave-length the largest effect is shown by iron for which $\Delta\mu/\mu$ is about 1 part in 1,000 when H is perpendicular[1] to X. For H parallel to X, Fig. 19 shows that the change is much smaller,[1] which may be partly due to the large demagnetizing field for such a thin sheet of iron. Of the other materials examined carbon and aluminum show the largest change. Nickel, platinum, copper, zinc and silver show changes smaller than 3 parts in 10,000 for either direction of H. At a mean wave-length in the neighborhood of 1.2 Å., wood shows a change in absorption of about 8 parts in 1,000 for H parallel to x-rays.

The following list sums up the values of $\Delta\mu/\mu$[2] together with an estimated probable error. The conditions under which each value was obtained can be found in the figures or in the legend for the figures. The estimate of the probable error is based on the oscillations of δ, the value of $\Delta I/I$ due to H for no absorber, and on the author's experience and judgment of the likelihood of small spurious effects.

All results are expressed in number of parts change in 10,000, a plus sign meaning an increase in μ.

For H perpendicular to X rays:

Iron $- 10 \pm 2$,
Copper $+ 0.8 \pm 0.4$
Carbon $- 5.6 \pm 2$,
Nickel $+ 1.6 \pm 0.5$,
Zinc $- 1.2 \pm 0.4$,
Aluminum $+ 8 \pm 6$.
Platinum $+ 1.7 \pm 0.4$,
Silver $+ 1.6 \pm 0.8$,

---

[1] Opposite to Forman's results.

[2] Corrected for a small effect observed with no absorber, which was never greater than 2 parts in 10,000.

For H parallel to X rays:

Iron − 0.5 ± 2,
Copper + 1.4 ± 1,
Aluminum + 2.7 ± 1,
Nickel + 0.7 ± 2,
Zinc + 1.3 ± 1,
Wood (longer wave-lengths) + 80 ± 20.
Platinum + 1.1 ± 1,
Carbon + 3 ± 1,

DISCUSSION OF RESULTS.

These results are in accord with the hypothesis that magnetic properties are largely conditioned by the outer atomic shell or valency electrons. If the magnetic fields inside the atom are actually as large as is supposed, we cannot hope to penetrate deeply into the atom with external fields. Consequently we should hardly expect to produce any changes in the inner shells. Now it is generally believed that the K absorption and emission are associated with the innermost shell while the L and M radiations are due to the next two shells of electrons respectively. Professor Richtmyer[1] has shown that very probably for wave-lengths less than the K_α limit, by far the larger part of the absorption is used up in exciting the K fluorescent radiation, a small percentage of the energy absorbed, for example, let us say 5 per cent., excites the L fluorescence, and presumably even a much smaller percentage, let us say .5 per cent., goes to excite the M fluorescence. On the above hypothesis we should expect to be unable to affect the K and L absorption of all substances having three or more shells of electrons. To be specific, let us consider aluminum which on Langmuir's theory contains a K shell of 2 electrons, an L shell of 8 electrons, and an outer shell of 3 electrons. If the external magnetic field produces no change in the K and L absorption but as much as a 10 per cent. change in the absorption due to the outer shell, the change in the total absorption would amount to only .10 × .005 or 5 parts in 10,000. On the other hand, carbon which contains only 2 shells would on the same suppositions show a change in the total absorption equal to .10 × .05 or 5 parts in 1,000. We should also expect a larger change in the total absorption if the wave-length were longer than the K_α limit. Both of these expectations are supported by the fact that at a given wave-length carbon and aluminum show larger changes than the heavier elements (excepting possibly iron and nickel), and that wood shows larger changes at long than at short wave-lengths.

On Compton's theory of scattering we might look for an appreciable change in that part of the absorbed energy which is scattered. In the low atomic weight elements a large percentage—as much as 50 per cent.—of the absorbed energy goes into scattered radiation. This investigation shows that the change in the scattered radiation cannot exceed about 1 part in 1,000.

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[1] PHYS. REV., 18, 13–30, 1921.

The most hopeful region to work in seems to lie near the absorption limit of the outermost shell. The most promising materials are the ones in the first two groups of the periodic table. While the experimental difficulties in working in the neighborhood of 100 Å. are great, the author believes that it will be well worth the effort and hopes to have the opportunity of continuing the search in that direction.

In conclusion the author wishes to express his appreciation and gratitude for the ever helpful and never failing encouragement, inspiration and assistance received from Professor Richtmyer.

Cornell University,
Ithaca, New York,
March, 1922.

THE ACTION OF THE BOW IN STRINGED INSTRUMENTS.

BY K. C. KAR.

SYNOPSIS.

Motion of Points of a String near the Bowing Region.—Shadows of a small section of the horizontal string and of pins stuck in the bow were thrown on a vertical slit back of which a piece of photographic paper was moved. The resulting prints each show a saw tooth line due to the string, crossed by inclined straight lines due to the pins. Experiments were made with the bow one seventh, one tenth and one fourteenth of the length of the string from one end. In every case the speed of the points of the string is proportional to the distance from the near end. The point with a speed equal to that of the bow is called the zero point. With strong slow bowing the zero point is at the outer edge of the bow, but with lighter or faster bowing the zero point may be 2 cm. or more nearer the middle of the string. While the "wolf note" is sounding the zero point oscillates periodically with the beating; it may be stopped by increasing the pressure. The amplitude at the outer edge of the bow is proportional to the speed of the string at that point and hence will change as the zero point is shifted by variations of pressure, even when the bowing speed is constant.

INTRODUCTION.

HELMHOLTZ, referring to the particular case in which the motion of the bowed point is represented by two step zig-zag, remarks[1] that the velocity of the string, in the forward motion "appears to be equal to that of the bow." In later treatises[2] the velocity of the forward motion is stated to be equal or about equal to that of the bow. Recently Professor Raman has made an experiment[3] with his vitrograph (see Fig. 1) and has shown that the velocity of the bow is exactly equal to the velocity of the bowed point of the string in its forward motion. His conclusion was based on the fact that the record of the pin attached to the bow and that of the string are absolutely parallel. But we should note that the photograph taken by him does not represent the motion of the bowed point, but of one a little away from it.

Now in practice a bow is never applied at a point. Thus in dealing with the problem we are to take into account the length of the bowed region, which is generally about 1 cm. long. This brings us at once to the question as to which point of the string in the bowed region, if any, has the same velocity as the bow. These problems raised by Prof.

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[1] Sensations of Tone, p. 83.

[2] Lord Rayleigh's Theory of Sound, Vol. 1, and Barton's Text book of Sound, Art. 261.

[3] The Dynamical Theory of the Motion of Bowed Strings, Bulletin No. 11 of Indian Association.

Raman in his monograph[1] are solved by the following experiment made by the writer.

I am deeply indebted to Professor Raman at whose suggestion I took up the work.

Experiment.

The apparatus is shown in Fig. 1. An arc placed in front of the apparatus provides the necessary illumination. A photographic paper contained in a dark slide is arranged to slide in grooves within the wooden box, parallel to the string. A number of pins are fixed to the bow transversely so that when bowed near the slit *S*, the images of the pins moving with the velocity of the bow, fall on the photographic paper inside the vitrograph. The transverse vibration of the string is at the same time recorded on the photographic paper. It is therefore possible by this method tog et simultaneous records of the motion of the bow and of the vibration of a point on the string in the neighborhood of the bowed region.

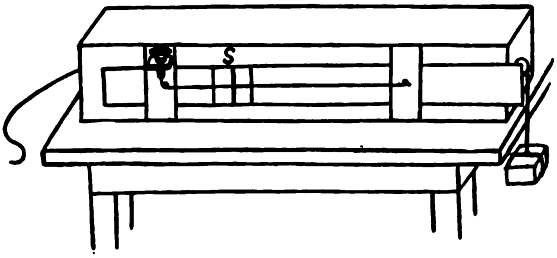

Fig. 1.

Exact determination of the point on the string whose vibrations have been recorded, is made by the following very simple method. A pin is held against the string and moved along it until its image falls on the slit. Vibrations of this point of the string have obviously been recorded. The distance of this point from one end of the string (here it is the remoter one) is measured with a meter scale. It should be noted that the position of the arc should not be changed during the experiment.

The inner and the outer limits[2] of the bowed region are marked with ink on the string. And by moving the slit to different positions, simultaneous records of the velocity of the bow and vibrations of different points of the string are taken. The bowing pressure has been made just sufficient to elicit a steady tone with pronounced fundamental, the velocity of the bow being kept constant as far as practicable. Three sets of records have been taken for three different positions of the bow.

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[1] Bulletin No. 15, Indian Association for the Cultivation of Science.

[2] The inner limit or the limit nearer the nearer end of the string.

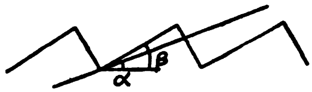

Fig. 2.

Records obtained are somewhat like that in Fig. 2. When the slit is placed anywhere between the inner edge of the bowed region and the nearer end of the string, angle β is always greater than angle α as in Fig. 2. When, however, the slit is on the other side of the bow, *i.e.*, away from the outer edge of the bowed region, β is generally less than α.

The ratios of the velocities of the string and the bow have been determined accurately from the records by measuring the tangents of the angles β and α with a moving microscope (moving in two perpendicular directions) and taking their ratios.

The results of these measurements are given in the following table:—

Table I

Length of the string is 53.6 cm.

	Bowed Region between.	Observed at	Vel. of String/Vel. of Bow Mean.
A.	45.55 cm.–46.45 cm.	42.1 cm.	1.358
		43.65 "	1.133
		47.40 "	.667
		49.20 "	.484
B.	47.65 cm.–48.55 cm.	48.90 "	.781
		49.40 "	.672
		47.0 "	1.116
		46.5 "	1.236
C.	49.3 cm.–50.25 cm.	48.3 "	1.273
		48.8 "	1.138
		50.8 "	.565

Conclusion.

It appears from curves (*B*) and (*C*) that the velocity of the string at the outer edge of the bowed region is the same as the velocity of the bow. But the curve (*A*) shows that the forward velocity of the string at a point away from the outer limit of the region is equal to the velocity of the bow. Thus the string in the bowed region, in this case, has smaller velocity than the

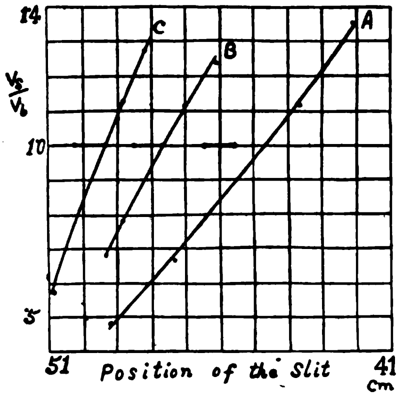

Fig. 3.

bow. The most important thing to be noted here is that the note emitted by the string is strong in the fundamental. This is shown by the photographs which are of simple Helmholtzian type of two step zig-zag. It is thus possible to get a steady fundamental when the forward velocity of the string in the bowed region is less than the velocity of the bow.

The curve (*A*) shows that the "zero point" (*i.e.*, the point which has forward velocity relative to the bow, equal to zero) is away from the outer edge of the bowed region. One would think it possible, by increasing the bowing pressure without increasing the velocity of the bow, to bring the "zero point" to the outer edge of the bowed region. This has been shown to be the case by a series of photographs, as in Fig. 4, of the simultaneous motion of the bow and of a particular point of the string away from the outer edge (2 cm. from it) with different bowing pressures. When the bowing pressure is small while the velocity of the bow is great[1] the "zero point" goes away from the outer edge towards the middle point of the string and the records of the pin and the string become parallel or very nearly so. When, however, the bowing pressure is greater while the velocity is smaller or nearly the same as before the "zero point" comes nearer the outer edge and the angle between the two records appreciably increases.

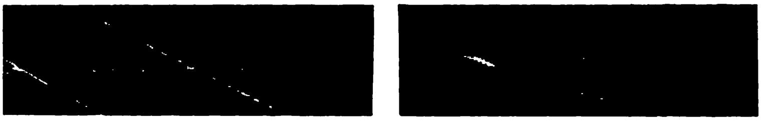

Fig. 4.

Thus the "zero point" may lie anywhere within a portion of the string, one of its limits being the outer edge of the bow. The other limit for which the vibration remains two step zig-zag of the first type has not been determined. But the photographs, taken, show that it may be at a distance of about 2 cm., if not more, from the outer edge. It should be noted, further, that the effect due to any increase of bowing pressure can be counterbalanced by a corresponding increase of the velocity of the bow. Thus it will be possible to have the "zero point" away from the outer edge even with a high pressure provided the velocity of the bow is correspondingly high. If then the velocity of the bow is increased keeping the bowing pressure constant or the bowing pressure is decreased keeping the velocity constant, the "zero point" goes away from the outer edge towards the middle point of the string and the intensity of the fundamental decreases until the octave becomes most prominent. This can be easily seen in the case of the mechanical violin-player of Dr. Raman.

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[1] The note emitted is strong in the fundamental.

In the case of two-step vibrations of the first type, the amplitude of oscillation of the string at the outer edge of the bowed region is given by $(1 - a/l)Tv$, where a is the distance of the point from the end and v its forward velocity, l being the length of the string. If the velocity of the bowed point were the same as the velocity of the bow (*i.e.*, $v =$ the velocity of the bow), as was supposed by Helmholtz and others, the amplitude of oscillation of the bowed point, *i.e.*, the intensity of the note emitted, would be independent of the bowing pressure, depending on the velocity of the bow. But it has been shown that the bowing pressure can change the value of v at the outer edge even when the velocity of the bow is constant. Thus the intensity of the note emitted can be varied slightly but appreciably, simply by varying the bowing pressure.

It will appear from the curves which are approximately straight lines that the nearer the bowed region is to the end the steeper is the curve, *i.e.*, the more rapid is the change in the forward velocity per unit length of the string within and near the bowed region. Thus the portion of the string in contact with the bow during vibration will be more and more inclined to a line perpendicular to the direction of bowing. And so a greater component of the frictional force will go to produce longitudinal vibration in the string. This effect is very marked when the bow is applied near the bridge.

Let us see if the results obtained are in agreement with what follows from dynamical considerations. It is obvious that the velocity of any portion of the string within the bowed region cannot be greater than that of the bow; for in that case the frictional force will act in the opposite direction and bring down its velocity to the velocity of the bow. Further it is not possible for every element of the string in the bowed region to have the same velocity as the bow. The "zero point" therefore, cannot lie within the bowed region or between the bow and the nearer end of the string as in that case a portion or the whole of the string in contact with the bow will have velocity greater than the bow which is not possible. So the only portion in which the zero point can lie is between the outer edge and the middle point. And this is exactly what the experiment shows.

The Wolf Note.

The results obtained throw some light on the nature of the "wolf note" [1] produced in bowed stringed instruments. It is evident from the photographs of wolf-note[2] that the inclinations of the line representing the forward motion of the string changes periodically, the period being the period of the wolf. From this it can be concluded that during the wolf the "zero point" oscillates periodically with the beating, though the pressure and velocity of the bow are constant. And it is only when, by increasing the bowing pressure, the "zero point" is fixed at the outer edge, that the wolf is controlled.

47 Corporation Street,
Calcutta,
November 14, 1921.

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[1] Dr. C. V. Raman pointed out in various papers (vide "On the Wolf Note in Bowed Stringed Instruments," Phil. Mag., 1916; also Bulletin No. 15 of the Indian Association) that at a particular pitch known as the wolf note pitch, a very peculiar beating note can be produced which however can be controlled by sufficiently large bowing pressure. He also showed that similar beating notes can be obtained at half the wolf note pitch. I have found that this sort of beating note can be obtained *e.g.*, in a violin at a large number of pitches, some of which are as strong as that at the wolf note pitch. They can, however, be controlled by increasing the bowing pressure. A little practice in bowing is necessary as some of them are produced by pressure varying within a small range.

[2] Bulletin No. 15, Indian Association for the Cultivation of Science.

A STUDY OF THE EFFECT OF ADSORBED GAS ON THE HIGH-FREQUENCY RESISTANCE OF COPPER WIRE.

By Austin Bailey.

Synopsis.

Effect of Adsorbed Gas on the High-frequency Resistance of a Loop of Copper Wire.—This resistance is known to be greater than would theoretically be expected if the surface layers have the same resistivity as the core. The experiments described were undertaken to determine whether this increased resistance is due to gas adsorbed by the surface layer of oxide. A square loop, 60 cm. on a side, was formed by enclosing copper wires inside of glass tubes connected to a vacuum pump, and after several hours' preliminary heating and pumping, the wire was glowed, and then its resistance for radio-waves of 20 meters length was found to increase in 20 minutes by several per cent., though the residual pressure was only 10^{-6} atm. After successive glowings the effect became progressively less as the oxide layer disappeared. With higher pressures the increase to an equilibrium value came more rapidly. These results indicate that the gas adsorbed by the copper-oxide layer does increase the resistance, and suggest that possibly copper wire whose surface is covered with a thin layer of metal such as tin, might have a lower high-frequency resistance than oxidized copper wire of the same size.

Short radio-waves, of less than 20 meters were produced by using only the capacity of the oscillating triode tube in the high-frequency circuit. The wave-length was measured to within ½ per cent. by use of a modified Lecher System, with a hot-wire galvanometer at a current loop. Currents in the square loop were measured by means of a loosely coupled circuit containing a special vacuum thermo-element with minimum coupling in the galvanometer circuit.

Adsorption of Gases by Copper Oxide and Copper.—The observations indicate that copper oxide readily absorbs gases at room temperature and liberates them when glowed, while copper does not.

An arc-type diffusion pump is described, which has an iron wire ballast resistance wound around the tube which conducts the vapor to the condensation chamber. This enables the pump to get into operation quickly.

Introduction.

At very short wave-lengths, measurements made of the high frequency resistance of a one meter square loop of wire show a much larger value than that calculated from the formula for the resistance of a straight wire of the same length. The comparison between the observed and calculated values of the resistance of a one meter square loop of No. 18 B. & S. gauge copper wire are shown in Fig. 1.

This discrepancy may be due to a number of causes, one of which may be gas adsorbed on the surface of the wire. Langmuir[1] has pointed out that there is probably a very close packing of the gas molecules adsorbed on the surface of a metal. Such a condensation would doubtless alter materially the physical properties of the surface. Since at high frequency, a large part of the current will flow in a thin skin near the surface, a change in the high-frequency resistance would be expected if we changed the properties of that surface.

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[1] I. Langmuir, Phys. Rev., *8*, 149 (1916).

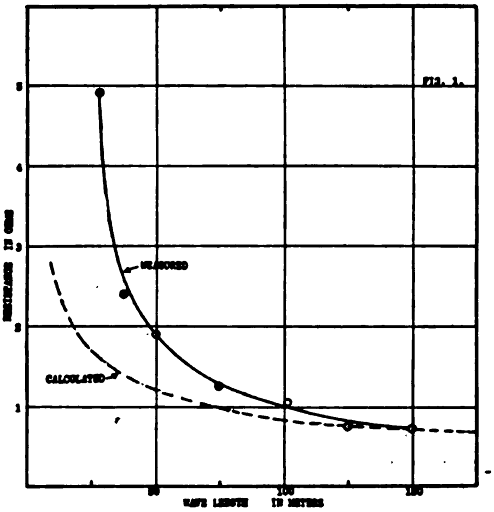

Fig. 1.

The experiments described below were undertaken in order to determine whether such a change of resistance due to a gas skin could be detected. The effect, if it exists, would be especially marked in some material which is known to adsorb gases strongly. Now Merton[1] has found that "copper strongly absorbs most gases." I, therefore, formed a square loop of copper wire, enclosing it in a glass tube so that the condition of the wire surface could be altered at will and measured the current flowing in the wire. A change in the resistance in the circuit, if capable of detection under the limitations of these experiments would then be indicated by a change in the reading of the galvanometer, since the electromotive force induced in the circuit was maintained constant.

TEST CIRCUIT.

The copper wire 0.045 cm. in diameter and about 240 cm. long was mounted at the center of a glass tube. The tube was made in two L sections which were so placed together as to form a square 64 cm. on each side, and were interconnected to the vacuum system as shown in Fig. 2. At the corner of each L tube the wire was supported by a Pyrex glass insulator *I*, connected at its far end to a spring *S*, which extended out into a small side arm which made equal angles with the sides of the L. By this means the wire was kept taut.

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[1] T. R. Merton, Chem. Soc. Jour., *105*, 645 (1914).

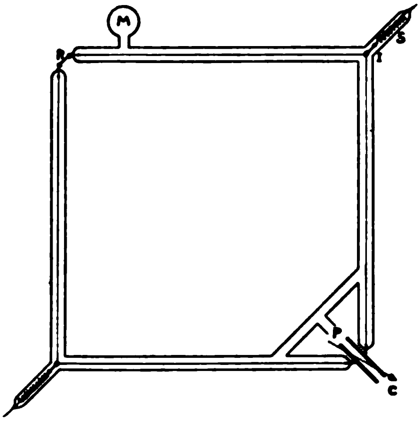

Fig. 2.

At the ends of each L the wire was attached to a piece of 1.05 mm. platinum wire and sealed out through the end, so that two of the corners of this square could be used for connecting additional apparatus. At one of these corners a single plate variable air condenser *C* was connected, and at the other corner an arrangement was made for connecting in various standard high frequency resistances, *R*, by means of mercury cups. Thus the resistance of the circuit could be measured by adding into the circuit known resistances.

Measuring Circuit.

To determine the change in current in the test circuit produced by different conditions of the wire, a circuit containing a 20 cm. loop of

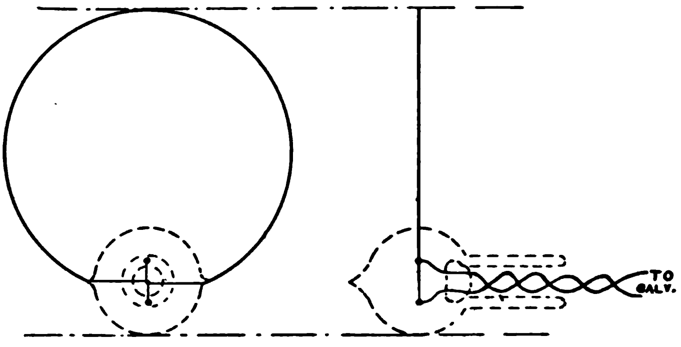

Fig. 3.

wire closed at its end by a thermo-element was inductively coupled to this circuit. The thermo-couple was especially designed and constructed so as to have as small currents as possible induced in the galvanometer circuit. This was done by making the plane of the loop at right angles to the galvanometer connections and by twisting together the insulated leads to the galvanometer as shown in Fig. 3. The copper-constantan element itself was mounted in a bulb which was evacuated to reduce thermal losses.[1] This increases the sensitiveness of the couple.[2] The measuring circuit being very sensitive could be loosely coupled to the test circuit and thus introduce only a very small resistance into the latter. At the same time it could be so placed that its loop plane was perpendicular to that of the oscillator circuit and thus reduce to a minimum direct action from the source of the power.

OSCILLATOR.

A three-electrode vacuum tube connected as shown in the diagram (Fig. 4) was used as a high-frequency generator.

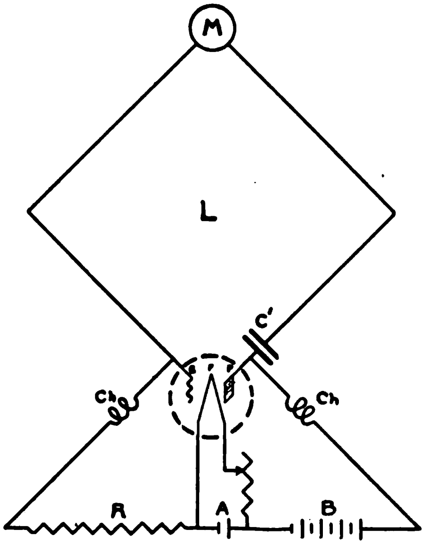

Fig. 4.

From the diagram it can be seen that the oscillating circuit contains only the capacity of the tube, in series with a blocking condenser C', of ½ μf. and the inductance of a loop of wire 100 cm. square, L. The hot-wire ammeter M is placed at a current loop so that it will indicate that the circuit is oscillating. The chokes Ch were so adjusted that they were resonant at a frequency slightly greater than the frequency generated by the oscillating circuit. Such an adjustment makes the chokes have a high inductive reactance at the frequency used, and prevents the high-frequency current from going back into the direct-current circuits. A negative potential of about 100 volts is maintained on the grid by means of the grid-leak resistance *R*. Any desired potential on the plate could be obtained by means of a potentiometer contact on a resistance, through which the current from a 300-volt generator was maintained constant by means of a ballast lamp. This circuit, with the exception of the power supply, was mounted on a movable base, so that the angle of the loop with reference to the test circuit could be altered by rotation about two axes. The coupling could also be changed by altering the position of the oscillator with reference to the test circuit.

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[1] I. Klemencic, Wied. Ann., *42*, 416 (1891).

[2] P. Lebedew, Ann. d. Phys., 4 s., *9*, 209 (1902).

MEASUREMENT OF FREQUENCY.

A wave-meter was made of a variable air condenser with a maximum capacity of 670 $\mu\mu$f. and a single loop of No. 10 B. & S. gauge copper wire 20 cm. in diameter. The resonance point was indicated by a hot-wire galvanometer inductively coupled to this. By courtesy of the Commanding Officer, Radio Laboratories, Camp Alfred Vail, New Jersey, use was made of the Lecher system of parallel wires, constructed there by the author during the war, for the purpose of calibrating the wave meter. In Fig. 5 is shown the arrangement of the circuit. The single-plate variable air condenser *C* was adjusted so that resonance with an outside source was obtained in the loop circuit. The resonance point was very sharp, due to the low resistance of the circuit, and was indicated by placing the hot-wire galvanometer at the point *B*. By this method the parallel wires were directly coupled to a circuit of fixed frequency and standing waves were produced on them. The wires were very long in comparison with the wave-lengths to be measured.

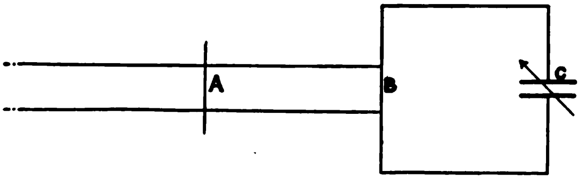

Fig. 5.

To measure the wave-length, a wire-bridge mounted on a long insulating handle was slid along the parallel wires until the hot-wire galvanometer at *B* showed a sudden decrease in reading to about half of its former value. Suppose this position was A, then the distance AB is some number of half wave-lengths. If the position A is the first such position found after leaving B, then AB is one half wave-length. A large number of current loops could be located in this manner, but since each position was more accurate than required, only two such determinations were made. While the method employed to determine the wave-length is similar to that described by Rubens,[1] the use of a small hot-wire galvanometer immediately at a current loop to indicate the positions of other current loops is believed to be of considerable advantage.

With an oscillating vacuum tube used to excite the system, the positions of A could easily be located so that the value of the wave-length thus determined was accurate within 0.5 per cent. The accuracy of this method for giving the correct indication of wave-length was checked down to 38 meters wave-length by a wave-meter composed of a standard inductance,[2] and a variable air condenser, both calibrated by the Bureau of Standards.

Vacuum System.

An oil pump which was capable of reducing the pressure to about 1 mm. of Hg was connected through a three-way stopcock to a drying tube containing P_2O_5. To the other end of the drying tube there was connected a system of two mercury condensation pumps in series. These pumps were made of Pyrex glass and connected by means of graded glass seal[3] to the McLeod gauge[4] and mercury trap. The design of the pumps is shown in Fig. 6. An arc[5] was used as the source of the vapor which was then conducted to the condensation chamber through a half-inch tube wound its entire length with No. 18 B. & S. gauge soft iron wire, with a cord, soaked in water-glass, wound between turns for insulation. To reduce the heat loss a covering of woven asbestos tape was wound on outside of the wire layer. The iron wire keeps the tube conducting the vapor warm[6] and at the same time acts as a ballast resistance for the arc. Tests made with this pump showed that its maximum rate of pumping was obtained when it consumed 300 watts and that the way in which this power was applied made no difference, *i.e.*, it could all be put into the arc, using external resistance, or it could be put into the arc and the resistance wound around the tube conducting the mercury vapor to the condensation chamber. The latter method of applying the power was, however, found to have the distinct advantage of making the pump effective sooner after closing the switch and at the same time of requiring a smaller current for operation.

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[1] H. Rubens, Wied. Ann., *42*, 154 (1891).

[2] Circular 74 of the Bureau of Standards, page 320.

[3] W. C. Taylor and Austin Bailey, Jour. Ind. Eng. Chem., *13*, 1158 (1921).

[4] Austin Bailey, Phys. Rev., *15*, 319 (1920).

[5] L. T. Jones and H. O. Russell, Phys. Rev., *10*, 301 (1917).

[6] Gaede, Ann. Phys., 4, 46, 357 (1915).

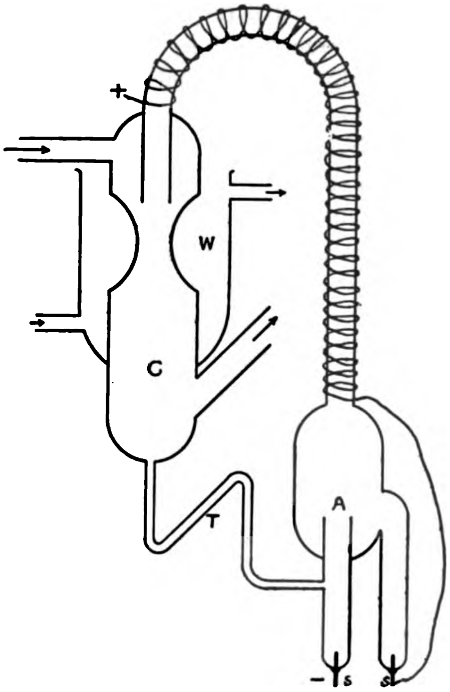

Fig. 6.

Observations and Conclusions.

With the apparatus arranged as described above, I first removed from the surface of the wire and the walls of the containing glass tube much of the adsorbed gas. This was accomplished by placing around the tube containing the wire an electrical resistance furnace and heating the glass to about 250° C., while at the same time the wire was raised to a much higher temperature by passing a current of about 2 amperes through it. This boiling-out process was continued for from three to four hours and then the tube containing the wire was sealed off from the pumping system. I then removed the furnace from the wire and allowed the apparatus to cool to the temperature of the room.

At the end of this process the surface of the wire was apparently covered with a layer of oxide. To remove any adsorbed gas from this surface layer, the wire was heated as hot as possible without burning out, and the observations begun immediately afterwards. The observations were continued until there appeared to be no further change in the resistance of the wire. Expansion of the wire caused by the increase in temperature, temporarily changed the inductance of the circuit. To compensate for this change, the circuit was constantly retuned during the cooling of the wire by adjusting the variable condenser *C* shown in Fig. 2. This adjustment was made at a distance from the circuit by means of a cord wound around the condenser handle, which enabled the observer to tune accurately without influencing the circuit by the close proximity of his body. The position of the observers remained fixed during each set of observations.

The attached curves show the results of several such runs. Fig. 7 shows successive runs on a wire which had previously been boiled out as described above. Two heatings of the wire to red heat were made to drive off adsorbed gas. This raised the pressure in the tube to about 4×10^{-3} mm. of Hg as indicated by the appearance of the discharge through the tube from a spark coil. One day later the wire was again heated red hot and beginning twenty minutes later the series of observations shown in Fig. 7 were made. The initial decrease in the resistance of the wire, shown by the rising portion of the curves, is obviously due to the cooling of the wire, for the tests made of the time required to obtain a maximum reading with the temperature of the test circuit constant proved that this gradual increase could not be due to the sluggishness of the measuring circuit. The subsequent decrease of reading is attributed to the readsorption of a film of gas by the oxide surface. As this takes place slowly at low pressures the galvanometer deflections go through a maximum, showing that the wire has a decreased resistance for a few

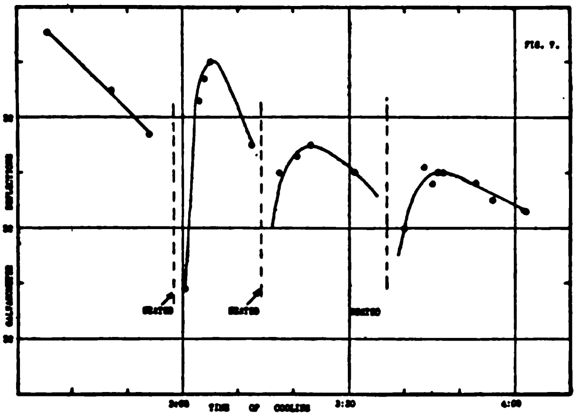

Fig. 7.

minutes after the wire has cooled and before the gas has had time to be completely readsorbed. The progressive decrease in the ordinates of successive curves in the series shown in Fig. 7 is probably due to the discharge of the storage battery of 40 amp.-hours' capacity which was running the motor-generator and discharging at an 8 amp. rate. The increase in the brightness of the appearance of the wire after successive heatings indicated that the flattening out of the maximum was probably due to the removal of the oxide covering, thus decreasing the asdorbing surface.

The same wire used in Fig. 7 was heated in the resistance furnace again for four hours at about 250° C. and the appearance of the wire surface changed from a bright copper color to a reddish brown, showing that the oxide layer which had been decomposed by the heatings previously given to it had been partially reformed. The behavior of this wire, plotted in Fig. 8, was similar to that shown in Fig. 7. No quantitative comparison can be made between these two figures or those following because of changes made in the position of the measuring circuit. Unfortunately the wire burned out during the third heating and a complete series could not be obtained.

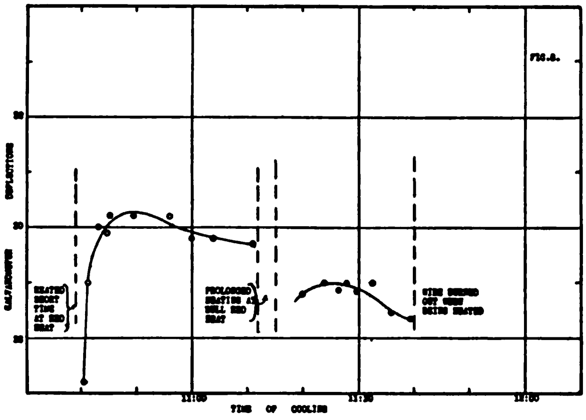

Fig. 8.

The curves plotted in Figs. 9 and 10 are made with a different wire. Previous to the first curve plotted in Fig. 9 the wire had been boiled out and sealed off in a tube, and had been allowed to stand several days. The pressure in this tube was not as low as in the tube previously used. An interval of 7½ hours elapsed before the first curve in Fig 9, during which time the storage battery was recharged. The curve following this charge of the storage battery is very erratic and full of accidental variations but it shows strong indication of a maximum. The next curve is more consistent in its points and fewer abrupt changes in galvanometer deflections were observed.

On allowing the air to again fill the tube at atmospheric pressure no marked change occurred. (See Fig. 9.) After heating the wire in air

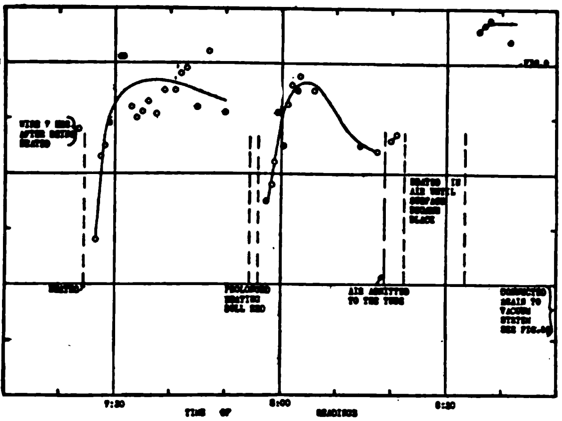

Fig. 9.

for ten minutes its surface appeared almost black, due undoubtedly to the formation of cupric oxide, CuO. Immediately after the heating current was turned off the oscillator was started again and observations made of the galvanometer deflections. These show a slight indication of a maximum. If this is a true maximum it is probably due to the same cause as before but is much sharper because the wire was initially at a lower temperature, could cool more quickly, and would probably readsorb gas more rapidly at atmospheric pressure.

The oscillator was again stopped, the tube connected to the vacuum

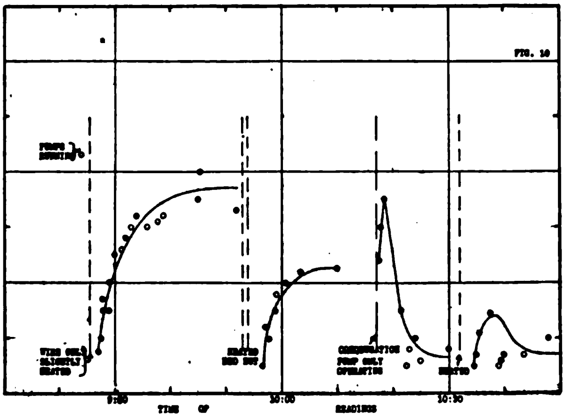

Fig. 10.

system and the pressure reduced to 3×10^{-4} mm. of Hg. The next two curves (Fig. 10) taken while the pumps were running, shows no maximum, probably because at this low pressure the gas was readsorbed more slowly by the oxide layer after heating. After the second heating at this low pressure the wire was apparently covered with the red oxide, Cu_2O. When the mercury condensation pumps were turned off and the backing pump still kept operating, the pressure gradually increased. The mercury in the pumps was so hot that it continued to go over and condense for some time after the current was turned off. This continued operation of the mercury pumps thus allowed the pressure to increase gradually. The first abrupt rise of the third curve shown in Fig. 10 may be due to some cause connected with stopping the operation of the mercury pumps, since the circuit at this frequency is very subject to variations from slight changes in nearby circuits. The final decrease of the galvanometer deflection however is probably due to the readsorption of the gas as the pressure increased.

Any single curve taken by itself would probably have little or no significance owing to the large fluctuations in the readings, due to accidental influences, but all the curves taken together strongly indicate: (1) that gas is readily adsorbed by copper oxide, and is easily liberated by heating, (2) that copper either does not adsorb gases as readily or that the adsorbed layer is not as easily liberated from the copper by heating, (3) that the resistance of the wire to high frequency currents is increased by the presence of the gas skin.

The "precipitated copper" as used by Merton was doubtless largely cuprous oxide as he describes it as "very dark brown in color," and as "prepared by reducing a solution of the copper salt." As is well known Cu_2O is prepared in this way. Finely divided copper can also be prepared in this way by the addition of suitable reducing agents such as $N_2H_4H_2O$. His statement that "if the copper is too strongly heated, it undergoes a change in color and loses its absorbing power," would also tend to show that the "precipitated copper" was largely Cu_2O and that on heating too strongly it underwent a chemical change, probably becoming metallic copper. Thus interpreted, his results are in entire agreement with the conclusions given above.

Copper wire when used commercially is doubtless covered with a thin layer of oxide, which strongly adsorbs gases, and which therefore according to the above results increases the resistance of the wire. Covering the surface of the wire with some metal which does not easily oxidize and at the same time does not appreciably adsorb gases would probably decrease the resistance of the wire. Possibly tin-covered copper wire would prove to have a lower high-frequency resistance than copper wire of the same size.

In closing, I wish to express my keen appreciation of the interest shown and encouragement given in this work by Professor Ernest Merritt and of the coöperation of Professor R. C. Gibbs in obtaining the material necessary to work out this problem. The advice and suggestions given by other members of the Department of Physics throughout the progress of this research is also greatly appreciated. Likewise, I wish to acknowledge the generous assistance which I have received from Professor Ernest Merritt and Doctor Gordon S. Fulcher in preparing this material for publication.

Cornell University,
June, 1920.

ELECTROMAGNETIC WAVES IN ABSORBING MEDIA.

By Leigh Page.

Synopsis.

Specific Intensities of Radiation in Two Media in Thermal Equilibrium.—If the media are transparent, the specific intensity of radiation K is proportional to the square of the index of refraction, as was shown by Kirchhoff. In dealing with absorbing media Planck assumes that K is proportional to the square of the real part of the complex index. Laue has questioned the validity of this assumption and has published an investigation of the problem purporting to show that K is proportional to the square of the modulus of the index of refraction. Laue, however, has treated incident and reflected waves in an absorbing medium as separate entities in computing energy fluxes, a method which is not legitimate when a change in phase occurs at reflection. The *mathematical investigation of the problem* given in this paper confirms Planck's assumed proportionality in the case of moderately absorbing media. In intensely absorbing media it is doubtful if it is legitimate to substitute trains of plane waves of equal intensity moving in all directions for the irregular fluxes due to emission and absorption in the medium.

Energy Flux for Homogeneous Plane Waves Incident on the Plane Surface of an Absorbing Medium.—Equations are derived for the energy reflected and the energy transmitted. On account of the difference in phase between incident and reflected waves the rate of absorption near the surface varies with the phase; in fact, it is negative for part of each period.

IN the theory of heat radiation it is of interest to investigate the relation between the specific intensities of radiation K of a given frequency in two media in thermal equilibrium with each other. The relation for the case of transparent media, given by Kirchhoff,[1] is obtained very easily. Let subscripts $_1$ and $_2$ refer to the two media and suppose the surface of separation to be smooth and plane. Then the energy of plane polarized waves incident at angle ϕ_1 (Fig. 1) in the first medium inside the conical angle $d\Omega_1$, per unit area of the surface of separation, per unit time, per unit frequency range, is

$$K_1 \cos \phi_1 \, d\Omega_1.$$

If r_1 is the coefficient of reflection, the energy reflected is

$$r_1^2 K_1 \cos \phi_1 \, d\Omega_1.$$

Hence the energy transmitted into the second medium is

$$(1 - r_1^2)K_1 \cos \phi_1 d\Omega_1 = (1 - r_1^2)K_1 \cos \phi_1 \sin \phi_1 d\phi_1 d\gamma, \qquad (1)$$

γ being the azimuth.

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[1] G. Kirchhoff, Gesammelte Abhandlungen, p. 594, 1882.

Equating to this a similar expression for the energy transmitted from the second into the first medium, and making use of Snell's law

$$\nu_1 \sin \phi_1 = \nu_2 \sin \phi_2,$$

where ν is the real index of refraction, it follows that

$$\frac{K_1\nu_2^2}{K_2\nu_1^2} = \frac{1 - r_2^2}{1 - r_1^2}. \tag{2}$$

But, the electromagnetic theory of light gives

$$r_1^2 = r_2^2.$$

Hence

$$\frac{K_1}{K_2} = \frac{\nu_1^2}{\nu_2^2}. \tag{3}$$

In his book on heat radiation,[1] Planck states this law in the form "the specific intensities of radiation of a certain frequency in the two media are in the inverse ratio of the squares of the velocities of propagation, or in the direct ratio of the squares of the indices of refraction," and, while his proof is limited to transparent media, he assumes that the result holds for absorbing media.

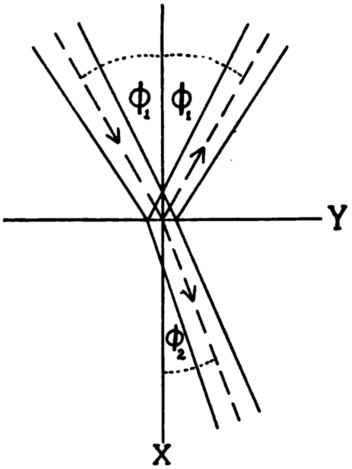

Fig. 1.

Laue[2] has questioned the validity of extending this relation to the case of absorbing media, and concludes that in this case the ratio should be that of the squares of the *moduli* of the complex indices of refraction, instead of the squares of the *real parts* of these indices, as Planck implies. The difficulty in using Planck's method of derivation in the case of absorbing media lies in the fact that except in special cases a homogeneous plane wave incident in one medium will be transmitted into the other as an unhomogeneous plane wave. In the latter type of wave the flux of energy is not continuously along the wave normal, but varies in direction as the phase changes. Hence the energy in the refracted wave is scattered, and Snell's law cannot be applied.

Laue's method of attacking the problem is this. He considers first equilibrium between two media whose indices of refraction have the same arguments but different moduli for waves of the particular frequency under consideration. In this case a homogeneous plane wave in one medium will remain homogeneous on passing into the other, and hence the method of derivation used by Planck for transparent media applies. For if the complex absolute index of refraction is denoted by

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[1] The Theory of Heat Radiation (Masius), p. 35, 1914.

[2] Ann. d. Phys., 32, 1085, 1910.

$$N = ne^{i\psi} = \nu(1 + ix),$$

then the relative index

$$\frac{N_1}{N_2} = \frac{n_1}{n_2},$$

will be real for equal ψ's in the two media. Hence in place of (3) is obtained the relation

$$\frac{K_1}{K_2} = \frac{n_1^2}{n_2^2}. \tag{4}$$

In order to find out how this relation involves the argument of the index, Laue next considers two media (one may be vacuum) whose indices of refraction have the same moduli but different arguments. He assumes that the irregular radiation passing through any point of the medium is equivalent to trains of homogeneous plane waves of equal intensity traveling in all directions, insofar as the average flux of energy is concerned. Then he takes expression (1) for the energy transmitted through the surface, where r is the modulus of the now complex coefficient of reflection. Integrating over a hemisphere he gets an expression for the energy transmitted from the first medium into the second. By the same procedure a corresponding expression is obtained for the energy flowing through the surface from the second medium into the first. In the state of equilibrium these expressions must be equal. But the integrands are the same, and as there is no total reflection the limits of the two integrals are the same. Hence

$$\frac{K_1}{K_2} = 1, \tag{5}$$

and Laue concludes that the ratio of the specific intensities is not a function of the arguments of the indices of refraction of the media. Hence, in general, this ratio must equal the ratio of the squares of the moduli, whereas Planck has assumed it equal to the ratio ot the squares of the real parts of the indices of refraction.

Laue's method is open to objection on the score that it is not obviously legitimate to replace the irregular radiation produced by absorption and reëmission in a medium which is not transparent by trains of homogeneous plane waves of equal intensity moving in all directions. This ideal condition, which must be assumed in order that the mathematical analysis of the problem may not become hopelessly involved, would seem to be less permissible the more strongly absorbing the medium, and the shorter the distance waves can proceed from their sources without being greatly reduced in intensity.

However, a closer examination of the problem does not confirm Laue's conclusion that the ratio of the specific intensities of radiation is independent of the arguments of the indices of refraction even when his method of analysis is followed. For Laue has assumed that incident and reflected waves in an absorbing medium may be treated as separate entities in computing the energy transmitted across the surface. This assumption would be legitimate if there were no change in phase on reflection. The change in phase, however, results in a transmission through the surface of an amount of energy greater than the difference between that brought up in the incident wave and that taken away in the reflected wave. This is in no way contradictory to the principle of conservation of energy, as the energy absorbed near the surface supplies the excess of energy transmitted over that accounted for by the difference of incident and reflected energies.

The object of this paper is to investigate by Laue's method the ratio of the specific intensities in two media which have the same moduli but different arguments in their indices of refraction. Without loss of generality one of the media may be assumed to be vacuum. The modulus of the index of refraction of the other, then, will be unity. It is shown below that for *moderately* absorbing media, Laue's equation (5) should be

$$\frac{K_1}{K} = \cos^2 \psi_1, \tag{6}$$

where K refers to vacuum. Hence combining with (4), it is seen that in the general case where both moduli and arguments differ in the two media,

$$\frac{K_1}{K_2} = \frac{n_1{}^2 \cos^2 \psi_1{}^2}{n_2{}^2 \cos^2 \psi_2} = \frac{\nu_1{}^2}{\nu_2{}^2}, \tag{7}$$

which is the relation deduced by Kirchhoff and Planck for transparent media. Hence Planck's extension of this relation to absorbing media is justified, at least for the case of *moderate* absorption. In the case of intensely absorbing media, it is doubtful if the substitution of trains of homogeneous plane waves for the energy fluxes actually present is legitimate.

Consider a homogeneous plane wave proceeding through an absorbing medium in the direction of the X-axis. Let the electric vector E and displacement D have the direction of the Y-axis. Then the magnetic vector H will lie along the Z-axis. If $\omega/2\pi$ is the frequency of the radiation, and S stands for the wave slowness *in vacuo*, the electromagnetic equations give

$$\begin{aligned} E &= Ae^{-\omega n \sin \psi Sx} e^{i\omega(n \cos \psi Sx - t)}, \\ H &= Ane^{-\omega n \sin \psi Sx} e^{i[\omega(n \cos \psi Sx - t) + \psi]}, \\ D &= An^2 e^{-\omega n \sin \psi Sx} e^{i[\omega(n \cos \psi Sx - t) + 2\psi]}. \end{aligned}$$

The Poynting flux is continuously in the X direction and amounts to

$$\begin{aligned} s &= cEH \\ &= \tfrac{1}{2} cA^2 n e^{-2\omega n \sin \psi Sx} \{\cos \psi + \cos [2\omega(n \cos \psi Sx - t) + \psi]\}, \end{aligned} \tag{8}$$

and the energy density

$$\begin{aligned} u &= \int E\dot{D}dt + \tfrac{1}{2}H^2 \\ &= \tfrac{1}{2} A^2 n^2 e^{-2\omega n \sin \psi Sx} [\cos \psi \{\cos \psi + \cos [2\omega(n \cos \psi Sx - t) + \psi]\} \\ &\qquad + \sin \psi \{2\omega t \cos \psi - \sin [2\omega(n \cos \psi Sx - t) + \psi]\}]. \end{aligned} \tag{9}$$

But the energy propagated in the form of waves must be equal to the Poynting flux divided by the velocity of propagation q, that is,

$$\begin{aligned} u_1 &= \frac{s}{q} \\ &= \frac{n \cos \psi}{c} s \\ &= \tfrac{1}{2} A^2 n^2 e^{-2\omega n \sin \psi Sx} \cos \psi \{\cos \psi + \cos [2\omega(n \cos \psi Sx - t) + \psi]\}, \end{aligned} \tag{10}$$

and, as the coefficient of absorption is evidently

$$\alpha = 2\omega n \sin \psi S,$$

the energy absorbed is

$$\begin{aligned} u_2 &= \int \alpha u_1 q dt \\ &= \tfrac{1}{2} A^2 n^2 e^{-2\omega n \sin \psi Sx} \sin \psi \{2\omega t \cos \psi - \sin [2\omega(n \cos \psi Sx - t) + \psi]\}. \end{aligned} \tag{11}$$

The sum of u_1 and u_2 checks with u, as it should.

Now it appears from (11) that the rate of absorption is not the same at different points along the wave, but varies with the phase. Fig. 2 is a graph of E, H, D, u_1 and s. The curve giving the rate of absorption of energy has the same form as that for the energy u_1 propagated by the wave. It will be noted that this curve lies below the horizontal axis wherever E and H have opposite signs. In these regions the rate of absorption is negative, that is, the medium is returning to the wave energy previously absorbed.

Consider now a train of homogeneous plane waves incident in the absorbing medium 1 (Fig. 1) at the angle ϕ_1. This medium has an index of refraction with unit modulus, *i.e.*, n is unity. Medium 2 is vacuum, and quantities referring to it will be denoted by letters without subscripts.

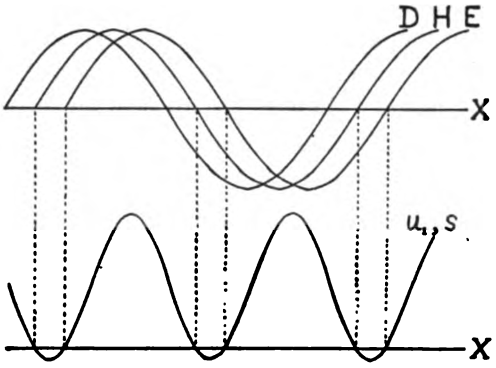

Fig. 2.

Confining attention to plane polarized waves with the electric vector normal to the plane of incidence, at the surface

$$
\begin{aligned}
E_{1_z} &= A_1 e^{i\omega(\cos\psi_1 S_y \sin\phi_1 - t)},\\
H_{1_x} &= A_1 \sin\phi_1 e^{i[\omega(\cos\psi_1 S_y \sin\phi_1 - t)+\psi_1]},\\
H_{1_y} &= -A_1 \cos\phi_1 e^{i[\omega(\cos\psi_1 S_y \sin\phi_1 - t)+\psi_1]},
\end{aligned}
$$

in the incident wave. The complex coefficient of reflection may be written

$$R_{1_\perp} = r_{1_\perp} e^{i\vartheta_{1\perp}}.$$

Then in the reflected wave

$$
\begin{aligned}
E_{1_z}' &= r_{1_\perp} A_1 e^{i[\omega(\cos\psi_1 S_y \sin\phi_1 - t)+\theta_{1\perp}]},\\
H_{1_x}' &= r_{1_\perp} A_1 \sin\phi_1 e^{i[\omega(\cos\psi_1 S_y \sin\phi_1 - t)+\psi_1+\theta_{1\perp}]},\\
H_{1_y}' &= r_{1_\perp} A_1 \cos\phi_1 e^{i[\omega(\cos\psi_1 S_y \sin\phi_1 - t)+\psi_1+\theta_{1\perp}]}.
\end{aligned}
$$

Now, the flux of energy through the surface is

$$s_{1_x} = -c[E_{1_z}H_{1_y} + E_{1_z}'H_{1_y}' + E_{1_z}H_{1_y}' + E_{1_z}'H_{1_y}].$$

If there were no change in phase on reflection the last two terms in the brackets would be equal and opposite in sign. Laue's result is due to his omission of these terms.

Substituting the values of the electric and magnetic intensities, and averaging over a period,

$$\bar{s}_{1_x} = \tfrac{1}{2} c A_1^2 \cos\phi_1 \cos\psi_1[(1 - r_{1_\perp}^2) + 2r_{1_\perp} \sin\theta_{1_\perp} \tan\psi_1]. \qquad (12)$$

The first term represents the difference between the energy brought up by the incident waves and that carried away by the reflected waves; the last term represents energy which had previously been absorbed by the medium close to the surface and is now transmitted across the surface into the vacuum in the form of waves. In fact, an investigation of absorption near the surface shows that the phase relation between reflected and incident waves is such that more than the average absorption occurs in this region. This excess absorption just accounts for the excess energy transmitted across the surface.

For waves with the electric vector in the plane of incidence, the same method of investigation gives[1]

$$\bar{s}_{1_x} = \tfrac{1}{2}cA_1^2 \cos\phi_1 \cos\psi_1[(1 - r_{1_{||}}^2) - 2r_{1_{||}} \sin\theta_{1_{||}} \tan\psi_1]. \qquad (13)$$

Now

$$\tfrac{1}{2}cA_1^2 \cos\psi_1 = K_1 \sin\phi_1 d\phi_1 d\gamma.$$

Therefore, taking both states of polarization into account, and integrating over a hemisphere, the total energy passing from the medium into the vacuum is

$$\bar{s}_{1_x} = 2\pi K_1 \int_0^{\pi/2} \cos\phi_1 \sin\phi_1 d\phi_1[(2^2 - r_1{}^2{}_\perp - r_{1_{||}}^2) + 2\tan\psi_1 (r_{1_\perp} \sin\theta_{1_\perp} - r_{1_{||}} \sin\theta_{1_{||}})].$$

Calculating the coefficients of reflection and substituting their values in this expression

$$s_{1_x} = 8\pi K_1 \sec\psi_1 \int_0^{\pi/2} c\cos^2\phi_1 \sin\phi_1 d\phi_1 \left\{ \frac{\cos d}{\cos^2\phi_1 + c^2 + 2c\cos\phi_1\cos(\psi_1 - d)} + \frac{\cos d}{\cos^2\phi_1 + c^2 + 2c\cos\phi_1\cos(\psi_1 + d)} \right\}, \qquad (14)$$

where

$$ce^{id}$$

is the complex cosine of refraction.

Following the same procedure in calculating the energy passing from the vacuum into the medium, the final terms in the expressions corresponding to (12) and (13) are absent as ψ is zero. In this case the total flux is

$$\bar{s}_x = 8\pi K \int_0^{\pi/2} c_1\cos^2\phi \sin\phi d\phi \left\{ \frac{\cos(\psi_1 + d_1)}{\cos^2\phi + c_1^2 + 2c_1\cos\phi\cos(\psi_1 + d_1)} + \frac{\cos(\psi_1 - d_1)}{\cos^2\phi + c_1^2 + 2c_1\cos\phi\cos(\psi_1 - d_1)} \right\}$$

---

[1] As $r_{1_{||}} \sin\theta_{1_{||}}$ is negative, the last term in (13) is positive.

$$
\begin{aligned}
= 8\pi K\Bigg[\cos\psi_1\int_0^{\pi/2} c_1\cos^2\phi\sin\phi\,d\phi\Bigg\{&\frac{\cos d_1}{\cos^2\phi + c_1^2 + 2c_1\cos\phi\cos(\psi_1 + d_1)} \\
&+\frac{\cos d_1}{\cos^2\phi + c_1^2 + 2c_1\cos\phi\cos(\psi_1 - d_1)}\Bigg\} \\
- 4\sin^2\psi_1\int_0^{\pi/2}&\frac{c_1^2\sin^2 d_1\cos^3\phi\sin\phi\,d\phi}{[\cos^2\phi+c_1^2+2c_1\cos\phi\cos(\psi_1+d_1)][\cos^2\phi+c_1^2+2c_1\cos\phi\cos(\psi_1-d_1)]}\Bigg] \qquad (15)
\end{aligned}
$$

Now, as $\sin d_1$ is of the order of $\sin\psi_1$, the last integral in (15) is of an order not less than $\sin^4\psi_1$ as compared with the first. Hence in the case of moderately absorbing media it can be neglected.

It can easily be shown that when ϕ_1 equals ϕ, $c = c_1$ and $d = -d_1$. Hence the integrand in (14) is identical with that of the first integral in (15) for equal values of ϕ_1 and ϕ. Equating these two expressions and canceling the equal integrals, equation (6) is obtained for moderately absorbing media.

The writer is indebted to Mr. N. I. Adams for calling his attention to the limitation of Planck's deduction of the relation between the specific intensities of radiation to the case of transparent media.

Sloane Physics Laboratory,
April, 1922.

A TRANSITION OR ADSORPTION-LAYER THEORY OF THE E.M.F. OF THE VOLTAIC CELL.

BY R. D. KLEEMAN.

12

SYNOPSIS.

Transition-Layer Theory of the Difference of Potential between an Electrolyte and a Metal Plate Immersed in It.—Since the layer of solution adjacent to the plate is under the influence of the molecular forces of the metal plate on one side and under those of the liquid on the other, it will, in general, differ from the rest of the solution in density, in concentration of solute (adsorption), and in degree of dissociation; and because of the difference in the diffusion velocities of the positive and negative ions, a segregation of the ions will result which will produce an electric field through the layer and will also charge the plate and the solution oppositely. These two fields, one due to the asymmetrical distribution of ions (volume charge) and the other to the charge on the plate, together cause the potential difference observed between metal and solution. The theory explains the well-known phenomena of the voltaic cell and also leads to the *prediction of a number of new effects*. When equilibrium exists the rates of gain and of loss of charge, by diffusion of ions to the plate and by chemical action, must be equal. This equilibrium should take an appreciable time to establish initially, it should be affected by a magnetic field and should be different if there is relative motion between the plate and the liquid. Also, if this theory is correct, the e.m.f. of a voltaic cell should depend on the distance apart of the plates and should change when a direct or alternating current is sent through the cell; and two rods of the same metal but of different diameters should show a difference of potential when dipped in the same electrolyte. These effects will be looked for experimentally. The *general differential equations* for the difference of potential according to this theory are given, but contain various functions whose form is at present unknown.

Transition layer at the free surface of a liquid should show not only an adsorption effect but also a segregation of the charges which may be associated with the *electrical effects of bubbling through liquid.*

NUMEROUS theories have been proposed to explain the nature of the e.m.f. of a cell. The most successful one that has of late been proposed is that by Nernst. Briefly his theory may be stated as follows: When a metal is in contact with a liquid there exists a tendency of the metal to go into solution in an electrified condition, which would leave the metal plate oppositely charged. The magnitude of this tendency, which is measured by what Nernst calls the solution pressure of the ions, depends on the nature of the metal and the liquid or solution. Therefore, if two different metals are placed in the same liquid, or solution, a difference of potential may exist between them, which would give rise to the flow of an electric current on joining the plates by a wire. Qualitatively the theory explains well such cells as the Daniel, and cells of a similar nature, but fails to do so in other cases without the introduction of additional hypotheses, especially in those cases where the metal does not appear to go appreciably into solution and the action of the cell is attended by the evolution of gases on the metal plates. Quantitative agreement of the formulæ deduced from the theory has been obtained only in special cases. It appears, therefore, that Nernst's theory of the e.m.f. of a cell requires modification, or that a new theory should take its place. It is evident or obvious on general chemical grounds that a metal in a liquid would tend to go into solution. But this might be a purely secondary effect as far as the production of an e.m.f. is concerned. In fact I will show that this is the case. A theory can be formulated which, as I will show in this paper, explains the production of an e.m.f. in all cases, by reference to well-known effects, and which indicates the existence of many interesting and important associated and subsidiary effects.

Let us consider a liquid or a solution in contact with a metal plate. Since the density of the metal is not likely to be the same as that of the liquid—in most cases it would be greater, the attraction exerted by an element of matter of the plate on an element of matter of the liquid at a given distance, would be different in magnitude from that obtained if both elements of matter belonged to the liquid. Accordingly the layer of liquid in the immediate vicinity of the plate would be subjected to a set of forces of different magnitude than a layer at some distance from the plate. The density of the liquid near the plate would therefore be different from that in the interior of the liquid, in fact, it would gradually change on passing from the immediate vicinity of the plate into the interior of the liquid. Since the attraction between two elements of matter decreases very rapidly with the increase of their distance of separation, the greater part of this change would take place in a very thin layer next to the plate which accordingly may be called the transition layer of the liquid. The thickness of the layer may be, however, it is of importance to point out, many times greater than the distance between two elements of matter at which the force they exert upon each other ceases to be of appreciable magnitude. It is evident that a modified layer of liquid will exist in the immediate vicinity of the plate whose thickness is at least equal to the radius of the sphere of action of a molecule of the plate. Another modified layer of liquid will exist adjacent to the first layer, since it is bounded on one side by a modified layer. The thickness of the second layer is equal to the radius of the sphere of action of a liquid molecule. A third modified layer will exist adjacent to the second layer, and so on. These layers will differ, the less from each other, the greater the distance from the plate, and at a certain distance, which may be taken as the thickness of the total layer, the state of the liquid will not differ appreciably from that at a great distance from the plate.

The liquid in the transition layer will differ in other respects than density from the other parts of the liquid. Thus if the liquid is a solution the ratio of the mass of solute to solvent will vary from one plane in the layer to another, and differ on the whole from the ratio in the remaining part of the solution. This effect is well known and is called adsorption. In the case that the solute is an electrolyte other important effects may occur, which would give rise to an e.m.f. across the layer. According to the theory of dissociation, a number γ of neutral molecules in the solution dissociate into ions each second. This number depends on the density of the solution, the concentration of the solute, and the temperature. It would, therefore, have different values in different parts of the transition layer. At the same time ions would become neutral molecules by recombination, the loss by recombination being equal to $\alpha n_1 n_2$, where n_1 and n_2 denote the concentrations of the positive and negative ions respectively, and α the coefficient of recombination. The value of α would also change from one part of the transition layer to another. If the rate of diffusion of the negative ions is different from that of the positive, as is usually the case, a partial separation of the ions of different signs will gradually take place. These rates of diffusion, it should be noted, will vary from one part of the layer to another, and will evidently depend on the direction of the diffusion with respect to the plate. In the immediate vicinity of the plate there is, therefore, likely to be a surplus of ions of one sign. The plate will accordingly become electrically charged through the motion of translation of the ions bringing them into contact with the plate, which effect is modified by the electrostatic attraction exerted by the plate on the ions. The sign of the electric charge on the plate very probably is the same as that of the ion which is in surplus near the plate. The plate will cease to charge up any further when the electrical gains and losses per second are equal. Corresponding to the charge on the plate an equal and opposite charge is distributed throughout the solution. This will give rise to an electrical field in the solution, which for convenience will be called the plate electrical field. The segregation of ions in the translation layer due to different migration velocities will give rise to another electric field which for convenience will be called the liquid transition layer field. Equilibrium exists when the migration of the ions under the action of the plate and transition layer electric fields, osmotic pressure, etc., is such that there is, on the whole, no gain or loss of ions in any part of the layer and solution. It should be observed that the plate electric field by itself cannot exist. For in that case the ions in the solution corresponding to the electric charge on plate would gradually be drawn towards the plate, and the electric field thus disappear. If, however, a tendency exists for the ions to segregate in the solution so that ions of opposite sign to the charge on plate tend to move away from the plate, the existence of the plate electric field would become possible. This is a very important point in the theory.

Thus the effect of the segregation of ions would be to produce an electric field, extending in the main from the outer boundary of the transition layer to the plate. It might be represented by two layers of electricity of opposite sign separated by a dielectric whose inductivity varies from layer to layer, and whose thickness is equal to the thickness of the transition-layer.[1] The change in potential experienced on passing an electric charge from the remote side of the layer to the plate is the difference of potential between plate and solution and may be called the transition-layer difference of potential. The magnitude of this potential will depend on the nature of the metal, the nature and the concentration of the solution, and the temperature, since the density of the transition layer, and the relative distribution of solvent and solute, would depend on the molecular forces exerted by the metal plate on the solution. Therefore when two different metal plates are placed in the same solution an e.m.f. would exist between them which would be equal to the algebraical sum of the e.m.f.'s of the two transition layers. Therefore when two different metal plates are joined by a wire a current would flow from one to the other returning through the solution.

It should be carefully noted that the electric field between plate and solution, and the corresponding difference of potential, consists of two distinct parts, one due to the electric charge on the plate, and the other due to an asymmetrical distribution of ions in the solution. The plate electric field, we have seen, may be said to be the outcome of the transition-layer field. But no definite relation need exist between their magnitudes. Thus it might happen that the latter field is small in comparison with the former. We would then be dealing with a state of affairs to which Nernst's solution pressure theory may be applied. It appears, therefore, that the theory proposed gives the "mechanism" of Nernst's theory in the cases where it can be applied. But the proposed theory goes a good deal further, namely, in explaining the difference of potential in all cases, including the important case when the metal shows no tendency to go into solution.

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[1] Resembling the Helmholz's interfacial condenser, whose apparent formation the theory would explain.

It will be of interest to examine a case of this particular case more closely—say plates of platinum and carbon immersed in a solution of sulphuric acid. A transition layer will be formed at the surface of each plate, and the partial segregation of the $+ H$, $- OH$, and $- SO_4$ ions, will give rise to a charging up of the plate without any metal necessarily going into solution, or any chemical change whatsoever taking place. The resultant differences of potential between the plates and the solution will not be the same since the transition layers will differ from each other on account of being bounded by different materials. On joining the plates by a wire a current will pass which will result in hydrogen being given off at one plate and oxygen at the other. Let us suppose that each plate gets completely covered by a layer of gas. If the gases were conductors of electricity like a metal the current would continue to flow but corresponding to a different difference of potential, since the liquid transition layers would now be bounded by plates of hydrogen and oxygen respectively. But on account of the non-conduction of the gases and the gradual obliteration of the liquid transition layers which are *in contact* with the plates, the current in practice will gradually decrease, and may stop altogether. This effect is known as polarization. It appears from the foregoing considerations that polarization in the various ways that it may occur can be strikingly explained by means of the proposed theory.

It will be of interest next to examine what happens according to the foregoing theory when a metal is immersed in a solution of an acid which dissolves the metal, say—a copper plate in a solution of H_2SO_4. The solutions will initially contain the ions $+ H$, $- OH$, and $- SO_4$, which are partly segregated in the transition layer adjacent to the plate. The motion of translation of the ions will bring some of them in contact with the plate, giving rise to the formation of copper oxide and copper sulphate, the latter dissolving in the solution. These ions will give their electrical charges to the plate. The $+ H$ and $- OH$ ions in coming in (proper) contact with the plate might give up their electrical charges without any chemical action taking place. The copper sulphate formed in the solution will give rise to the formation of $+ Cu$ and $- SO_4$ ions, and the electrical nature of the transition layer will undergo a corresponding change. This process will go on till equilibrium is reached, which corresponds to the number of copper atoms combining per second with $- SO_4$ ions being equal to the number of $+ Cu$ ions deposited on the plate. Now these numbers are evidently controlled by the electric field of the liquid transition layer and that due to the charge on the plate. Thus the ultimate concentration of the copper sulphate solution would be determined by the transition layer adjacent to the plate.

It will be of interest to point out that the free surface of a solution should possess a similar transition layer with which an e.m.f. would be associated. In such a case the density of the layer will obviously decrease on passing from its lower side to the upper side or surface of the liquid. This would have the effect of producing an adsorption effect (which is well known), and a segregation of the electrical charges similar to what takes place when the solution is in contact with a metal plate. This layer is probably intimately associated with the electrical effects produced by the bubbling of gases through liquids.

The distribution of the electrical charges in a transition layer may be predicted in a general way from the foregoing considerations. Let us consider a metal plate of infinite area in contact with a layer of solution of infinite thickness. If the difference between the concentration of the positive and negative ions, or $n_1 - n_2$, is measured along a line at right angles to the plate, and plotted against the distance from plate which will be denoted by x, a curve of the general form shown in Fig. 1 would be obtained from general considerations for the case that an excess of positive ions exists in the immediate vicinity of the plate. The ordinate corresponding to $x = 0$ gives the positive charge on the plate, while the ordinate corresponding to δx gives the excess of positive ions close to the plate. At the point $x = x_1$ the concentrations of the different ions are equal to each other, and at the point $x = x_2$ the excess of negative ions passes through a maximum. For greater values of x the excess of negative ions rapidly decreases, and when $x = \infty$ the excess is zero, the curve being asymptotic to the x axis at this point. It may happen in some cases that more than one maximum exists corresponding to $x = x_2$, and that maxima and minima may occur between $x = 0$ and $x = x_1$.

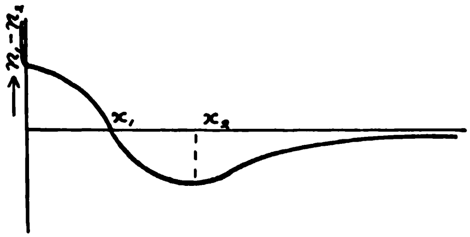

Fig. 1.

If an excess of negative ions occurs close to the plate, a similar state of affairs exists. We may then suppose that the curve represents the relation between $n_2 - n_1$ and x.

It appears from the foregoing results that if the layer of solution is infinitely thick, strictly speaking this holds also for the transition layer. But the greater part of the change in the layer evidently takes place over a small thickness, which may for convenience be taken to be equal to x_2 in Fig. 1.

If the concentration for each kind of electrical charge were plotted against distance from the plate two curves of the general form shown in Fig. 2, would be obtained. Each curve may, of course, have more than one maximum or minimum such as indicated.

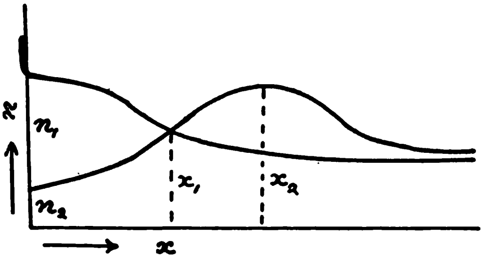

Fig. 2.

The differential equations of the transition layer may immediately be formulated. The electric field X acting towards the plate at any point in the layer is given by

$$X = \frac{4\pi\rho}{K},$$

where ρ denotes the density of the electric tubes of force, and K the inductivity of the liquid. On differentiating this equation with respect to x we have

$$\frac{dX}{dx} = \frac{4\pi}{K}\frac{d\rho}{dx} - \frac{4\pi\rho}{K^2}\frac{dK}{dx}$$

or

$$\frac{dX}{dx} = \frac{4\pi}{K}(n_1 - n_2)e - \frac{X}{K}\frac{dK}{dx}, \tag{1}$$

since

$$\frac{d\rho}{dx} = (n_1 - n_2)e,$$

where e denotes the charge on an ion. The current at right angles to the layer towards the plate, which is caused by the motion of the ions due to the action of the electric field, the action of the molecular forces, and the motion due to diffusion, is zero, and hence

$$(X + F_1)n_1e + eD_1\frac{dn_1}{dx} + (X - F_2)n_2e - eD_2\frac{dn_2}{dx} = 0, \tag{2}$$

where D_1 and D_2 denote the coefficients of diffusion of the positive and negative ions respectively, and F_1 and F_2 the forces respectively acting on the positive and negative ions toward the plate due to the asymmetrical distribution of the neutral molecules. The algebraical gain in ions of one sign per c.c. through diffusion, dissociation of neutral molecules, recombination of ions of different signs, and the velocity given to the ions by the electric field and molecular forces, is zero, and hence

$$d\frac{[(Xe + F_1)k_1n_1e]}{dx} - D_1\frac{d^2n_1}{dx^2} - \gamma + \alpha n_1n_2 = 0, \tag{3}$$

$$d\frac{[(Xe - F_2)k_2n_2e]}{dx} - D_2\frac{d^2n_2}{dx^2} - \gamma + \alpha n_1n_2 = 0, \tag{4}$$

where γ denotes the number of neutral molecules dissociating per c.c. into ions per second, α the coefficient of recombination, and k_1 and k_2 the mobilities of the positive and negative ions under unit force respectively. Since the total positive charge on plate and solution is equal to the negative we also have

$$\int_0^{x_a} n_1\cdot dx = \int_0^{x_a} n_2\cdot dx \tag{5}$$

if a slab of solution in contact with the plate of thickness x_a is considered.

The foregoing differential equations refer to the ions in the transition layer and the charge on the plate. The differential equations referring to the undissociated molecules of the solute are

$$F'N' + D'\frac{dN'}{dx} = 0, \tag{6}$$

$$d\frac{(F'k'N')}{dx} - D'\cdot\frac{d^2N'}{dx^2} + \gamma - \alpha n_1n_2 = 0, \tag{7}$$

where D' denotes the coefficient of diffusion of the molecules, N' their concentration, and k' the mobility of a molecule under the force F' due to the surrounding molecules and ions. The differential equations referring to the molecules of the solvent are

$$F''N'' + D''\frac{dN''}{dx} = 0, \tag{8}$$

$$d\frac{(F''k''N'')}{dx} - D''\frac{d^2N''}{dx^2} = 0, \tag{9}$$

where the meaning of the symbols F'', N'', k'', and D'', is obvious from the context. The quantities D_1, D_2, k_1, k_2, F_1, F_2, etc., depend on the density, etc., of the solution, and therefore on x. Since the forms of these functions are not known, the complete solution of the differential equations is obviously not immediately possible. But even if they were known a complete solution does not seem realizable except in special cases. The subject will be considered more fully in a separate paper, in connection with the experimental facts.

The e.m.f. between plate and solution will also be subject to thermodynamical conditions which involve the variables internal energy, tempterature, volume and external pressure. These conditions need not concern us here since the e.m.f. would be subject to them whatever its cause. This aspect of the subject will be found fully treated in Winkelmann's Handbuch des Physik, II. ed., pp. 801–814.

A few additional remarks should be made in connection with Nernst's solution pressure hypothesis. Nernst[1] has expressed the difference of potential E between a metal and solution in the form

$$E = -RT \log P_s + C,$$

where P_s denotes the osmotic pressure of the metal ions in the solution, and C an integration constant. The equation may also be written

$$E = RT \log \frac{P}{P_s}, \tag{10}$$

where P is of the nature of a pressure, and which has been called by Nernst the solution pressure of the metal, or the tendency of the metal to go into solution. But this tendency, we have seen, depends on the electric field of the liquid transition layer adjacent to the plate, which influences the collision of the ions of the solution with the metal. Thus in the proposed theory the nature and cause of an apparent solution pressure of a metal is the adjacent liquid transition layer.

The foregoing theory deals only, it should be noted, with the e.m.f. whose production and action is attended by chemical changes in the solution. The contact e.m.f. due to the differences in concentration of the free electrons in metals, etc., accordingly is not included. The e.m.f. of a cell as measured in practice is equal to the sum of these two electromotive forces. For the theory of the latter e.m.f. the reader may consult The Electron Theory of Matter by O. W. Richardson.

Some very important deductions can immediately be made from the foregoing theory of the e.m.f. of a voltaic cell without obtaining the solution of the differential equations of the e.m.f. of the transition layer. These will now be pointed out.

(*a*) Since according to Fig. 1 the transition layer is, strictly speaking, infinitely thick, the e.m.f. between two plates in a solution should depend to a certain extent on the distance between them.

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[1] Theoretische Chemie, by Walther Nernst, VII. ed., p. 784.

(*b*) An alternating current sent through the solution and plate should change the e.m.f. of the transition layer associated with the plate. The way in which this is brought about will best appear from considering a special case. Let us consider a solution of $CuSO_4$ in contact with a Cu plate, and let us suppose that an excess of Cu ions, which are positive, occur in the immediate vicinity of the plate, in which case the e.m.f. of the layer acts in a direction away from the plate. Therefore when the direction of the current is towards the plate copper will be deposited. On the current being reversed the copper deposited will not go into solution in the reverse manner. Copper will go into solution only as $CuSO_4$ through the interaction with $-$ SO_4 ions, and this solute will then gradually dissociate into $+$ Cu and $-$ SO_4 ions. Accordingly when the layer is in equilibrium the distribution of ions is different from that when no alternating current is flowing, and a corresponding change in the e.m f. of the transition layer would result. On breaking the current the layer would require a definite time to attain its original condition, which might be measurable.

A consequence of the foregoing result would be that the capillary electrometer should show a deflection under the action of an alternating current. It would also follow that the velocity of colloidal particles carried along by an electric current would experience a change in velocity on impressing an alternating current upon the direct current. An alternating current would also affect the precipitation of colloidal particles. Furthermore, electrical endosmose would be affected by a simultaneous application of an alternating current.

(*c*) A direct current sent through a transition layer would change its e.m.f. We have seen that the distribution of the ions in a transition layer is such that the velocity of migration of the positive ions, which is due to the action of the electric field, the molecular field, and diffusion, is equal to that of the negative ions at all points. Now when a direct current is sent through the layer an external field is impressed upon it, and hence a redistribution of electrical charges must result in order that the foregoing conditions may still hold. This would accordingly be attended by a change in the e.m.f. of the layer which exists apart from that due to the current.

On breaking the current it would take some time for the layer to regain its original distribution of electrical charges, and hence its original e.m.f. This might be made the basis for detecting the effect, and to a certain extent measuring it.

It follows from the foregoing result that the e.m.f. of a cell should change somewhat with the current furnished by it. The effect would evidently be the smaller the smaller the e.m.f. of the layer due to the passage of the current is in comparison with that due to a segregation of electrical charges.

(*d*) If a metal plate is suddenly plunged into a solution, the transition layer would not be formed instantaneously, but the process should take some time. Therefore, if two plates A_1 and A_2 of the same kind of metal were connected with a galvanometer, one plate to each terminal, and the plate A_1 be immersed in a solution for some time, a sudden deflection should be obtained on plunging the plate A_2 into the solution. This would be mainly due to the e.m.f. of the transition layer associated with the plate A since the layer of the plate A would take some time to form. The transition layer of air next to a plate before immersion may have an e.m.f. associated with it whose magnitude is not negligible in comparison with that of the liquid transition layer on immersion, in which case it would be necessary to work in a partial vacuum. The direction of the current obtained would in any case furnish interesting information in connection with the transition layer of each plate under various conditions.

(*e*) If one of the plates at the end of the foregoing experiment be removed from the solution for a time, a transition layer having an e.m.f. associated with it would gradually be formed on the *surface* of the solution adhering to the plate. Hence when the plate is suddenly returned to the solution a deflection would be obtained corresponding to the e.m.f. of the surface transition layer of the solution. The results obtained would be independent of the nature of the metal plates used.

(*f*) If two rods of the same material but different diameters be inserted into the same solution, the transition layers would not be the same in the two cases on account of the difference in radius of curvature of the rods. Hence an e.m.f. would exist between the two rods equal to the difference between the e.m.f.'s of the transition layers. It would, however, be of appreciable magnitude only if the radius of one of the rods is extremely small.

(*g*) The e.m.f. of a transition layer would obviously be affected by the application of an external pressure upon the solution. If this is done suddenly the e.m.f. of the layer might undergo a succession of interesting changes before equilibrium is reached due to the rearrangement of the electrical charges.

(*h*) The e.m.f. of a transition layer would be affected by a change in temperature, since this would change its density, etc.

(*i*) On giving a motion to a solution parallel to the surface of an immersed plate, a part (at least) of the transition layer associated with the plate would be carried along and be replaced by electrically unpolarized solution which in turn would tend to get more or less electrically polarized before it is itself carried away. Thus the e.m.f. of the transition layer would be different under these conditions from that existing when the liquid is at rest.

(*j*) A magnetic field applied to a plate immersed in a solution would change the e.m.f. of the transition layer, since it would affect the coefficients of diffusion of the different ions.

(*k*) The application of a stretching force to a metal plate immersed in a solution would change the e.m.f. of the transition layer. For such a treatment would change the molecular or atomic arrangement of the metal plate, and hence modify the forces exerted by the plate on the solution.

(*l*) The addition of a non electrolyte to a solution would change the e.m.f. of the transition layer, since this would change the values of D_1, D_2, k_1, k_2, F_1, F_2, etc.

The foregoing effects might be experimentally investigated in various ways. Investigations are at present in progress, the results of which will be published in subsequent papers.

The Physical Laboratory,
Union College,
Schenectady, N. Y.

THE VARIATION OF THE RESIDUAL IONIZATION IN AIR WITH PRESSURE, FOR A RANGE OF 57 ATMOSPHERES.[1]

By K. Melvina Downey.

Synopsis.

Residual Ionization in a Closed Spherical Steel Vessel One Foot in Diameter, for Pressures up to 58 Atmospheres.—The present work is an extension of previous experiments in which a linear relation was found between rate of ionization and pressure up to 22 atmospheres. Essentially the same method and apparatus was used as before. Results for air from 9 to 17 days old are given in curves. From 2 to 27 atmospheres, the rate of ionization increased linearly with the pressure at the rate of about 1.25 pairs of ions per c.c. per second per atmosphere change of pressure. Between 27 and 47 atmospheres the curves differ somewhat, the slope seeming to decrease with age, but above 47 atmospheres all curves are approximately horizontal, that is, the ionization was found to be practically independent of the pressure from 47 atmospheres up to the highest pressure tried. In view of the theoretical conclusions already established by Professor Swann this result clearly proves that the ionization due directly or indirectly to the action on the air of a penetrating cosmical or other radiation is extremely small, less than 0.1 pair of ions per c.c. per second at any pressure. Of the ionization produced at atmospheric pressure, about 1.25 pairs per c.c. per second must be due to radiations, either primary or secondary, coming from the walls of the vessel and having penetrations of from 28 to 47 ft. in air at atmospheric pressure; the rest must be due chiefly to much softer radiation, also from the walls. In the previous experiments performed outdoors over water instead of in the laboratory, the change of the rate of ionization with pressure was 1.56 instead of 1.25. The difference may be due to screening action by the laboratory building.

Ionization Due to the γ Rays of Radium in Air in a Closed Spherical Steel Vessel One Foot in Diameter, for Pressures Ranging up to 57 Atmospheres.—A curve obtained with 2 mg. of lead-shielded RaBr placed 8 feet from the vessel, shows a slope which constantly decreases as the pressure increases, the slope at 50 atmospheres being about one eighth of the slope at one atmosphere. Evidently most of the ionization is due to secondary radiation from the walls.

Introduction.

The present investigation is a continuation to higher pressures of a previous experiment,[2] in which the residual ionization in air in a sphere having an internal diameter of one foot was found to be a linear function of the pressure up to twenty-two atmospheres. The experiments were undertaken for the purpose of gaining information as to the type of radiation responsible for the residual ionization. The linear relation obtained would indicate that the ionization was due either to a direct action of an external radiation, or to a secondary corpuscular radiation emitted from the walls of the vessel and having a penetration of at least twenty-two feet at one atmosphere. The results obtained by other observers on "Residual Ionization" were discussed in the previous paper.

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[1] Presented at the annual meeting of the American Physical Society in Chicago, December 28–30, 1920.

[2] Phys. Rev., Vol. 16, pp. 420–437, 1920.

Apparatus and Method.

In the earlier work the central systems of two similar spherical ionization chambers were connected together and to a fiber electrometer, while the outer walls of the chambers were connected to opposite ends of a high potential battery. This battery was shunted with a resistance of ten megohms, and the midpoint of this resistance was connected to the case of the electrometer, in order to eliminate completely the effect of any fluctuations of the potential of the batteries. In the present experiments it was found advisable to replace the 10-megohm resistance by adjustable wire resistances immersed in oil as these remained more constant under rather trying conditions. Furthermore a sliding connection with the earth terminal was arranged so that, in case of any irregular changes in the various resistances, the earthing point[1] could easily be kept connected to the electrical midpoint of the resistances.

With a few exceptions, the details of the pressure arrangement were the same as in the earlier work. The pressure in one sphere was varied, while that in the other sphere was kept atmospheric. The pressures recorded in this paper refer to the excess over atmospheric just as in the previous paper. In the case of the high-pressure ionization sphere, it was necessary to replace the bolts holding the hemispheres together by bolts of larger cross-sectional area. During the course of the work, several imperfections appeared on the plane surfaces of the cross-sections of the hemispheres, so that considerable difficulty was experienced in finding suitable material for the gaskets. Copper was found unsatisfactory and rubber was finally resorted to.

The method of measurement differed in no essential way from that given in the previous paper. The capacity of the system was found to be 27.4 e.s. units.

Saturation Voltage.

Thorough tests for the saturation voltage were made. The potentials given to the ionization spheres and the corresponding values for q, the number of pairs of ions per c.c. per second, are shown in Table I.

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[1] It is convenient to speak of the common point to which all the shields, etc., were connected as the earthing point, although actual connection of this point to earth is, of course, unnecessary.

TABLE I.

Potential in Volts.	*q*		
	Pressure 52 Atmospheres.	Pressure 53 Atmospheres.	Pressure 56.7 Atmospheres.
120	42.4	42.4	
200	45.5	49.8	
320	50.4	50.4	
400	51.3	51.2	
520	51.5		
600	51.5	51.5	54.9
760	51.5		
800	——	51.7	54.8

It is evident from this table that 500 volts was ample for saturation. The potential on the spheres in the actual experimental work was from 700 to 800 volts.

RESIDUAL IONIZATION CURVES.

The graphs given in Figs. 1, 2, 3, 4 represent the change in residual ionization when the pressure excess over atmospheric was varied from zero to a value of the order of 57 atmospheres. A linear relation having a constant slope from one atmosphere to a pressure of the order of 27 atmospheres is shown by all four curves in agreement with the writer's former results. The decided drop in ionization below one atmosphere was undoubtedly due to easily absorbable radiation.

TABLE II.

Figure.	Age of Air.	Δq for *AB*.	Pressure at *B*.	Δq for *CD*.	Pressure at *D*.
I..............	17 days	1.23	27.7	0.58	45.6
II..............	14 "	1.31	26.3	0.70	46.5
III..............	10 "	1.20	26.3	0.84	47.0
IV..............	9 "	1.22	27.5	1.06	43.8
Average..........		1.25	27.0	0.79	45.7

The values for the change in the number of pairs of ions produced per c.c. per second for a change of pressure of one atmosphere are given for each of the curves in Table II., where they are designated by Δq. The air was left in cylinders for some time before each set of observations so as to allow radioactive emanation to decay, but, as will be seen from Table II., Δq shows no variation for the region *AB* of the curves for an increase of the time of ageing from 9 to 17 days. This confirms the

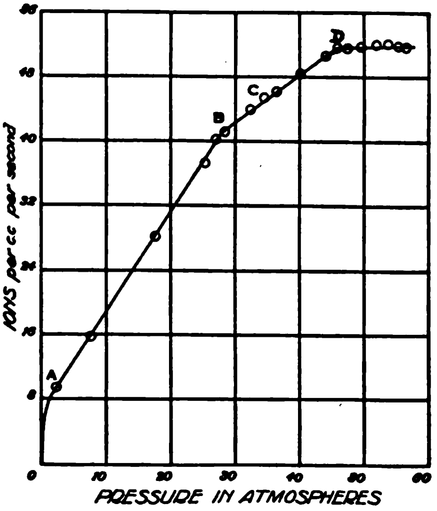

Fig. 1.

Residual ionization in air 17 days old.
1 P.M., Sept. 2, to 5:15 A.M., Sept. 3, 1920.

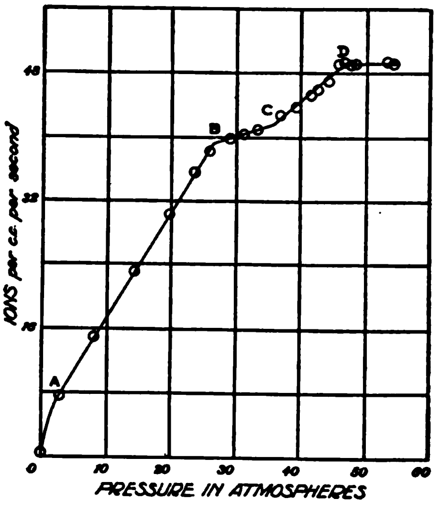

Fig. 2.

Residual ionization in air 14 days old.
4 P.M., Aug. 30, to 12 noon, Aug. 31, 1920.

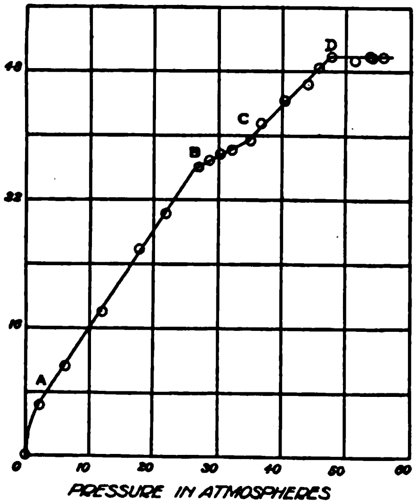

Fig. 3.

Residual ionization in air 10 days old.
5 P.M., Aug. 19, to 10 A.M., Aug. 20, 1920.

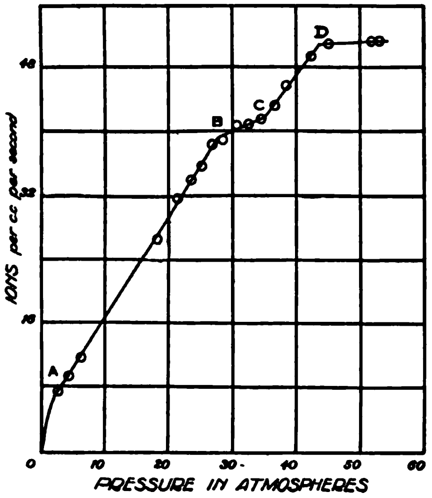

Fig. 4.

Residual ionization in air 9 days old.
10:50 A.M., Aug. 17, to 8 A.M., Aug. 18, 1920.

results of the preliminary experiments, for some of which the air was aged as long as 90 days. The effect of any small amount of emanation, which may be present, is masked then by the larger portion of soft radiation for the portion *AB* of the curve, but an examination of Δq for the portion *CD* gives a suggestion of an effect due to the emanation. (It may be noted that Curve IV., for which there was the shortest period of ageing, shows a greater deviation than any other curve from the average values in the last two columns of Table II.).

Emanation may also be in part responsible for the rather irregular changes in slope shown particularly by Curves 2, 3, and 4, which correspond to the smaller periods of ageing. This would seem probable because, before taking the readings at the higher pressures, it was not always possible to wait the required time for the old decay products of any emanation present to come into equilibrium with the new amount remaining after a part of the air was expelled. The result of this would be to cause the ionization after releasing the pressure to be greater than the normal value corresponding to the lower pressure. The difference would depend upon the interval elapsing between the change of pressure and the recording of the reading, and would consequently tend to cause more or less irregular changes in slope of the curve obtained. It is of interest to observe that these changes are conspicuously absent in the case of Curve 1, which corresponds to the longest period of ageing.

The curves agree in that they indicate an upper limit for the ionization, and this is attained at a pressure of the order of 46 or 47 atmospheres. The ionization was apparently constant for the remaining range of pressures tried (approximately 47 to 57 atmospheres). The *significance of the attainment of an upper limit* beyond which the ionization does not increase with further increase of pressure was pointed out by Professor W. F. G. Swann in a paper presented before the American Geophysical Union, Washington, D. C., April 18, 1921.[1] Professor Swann has shown that the minimum increase of ionization per c.c. per atmosphere, as measured for any pressure, is greater than any portion of the ionization per c.c. per second at one atmosphere, due to the direct action of a penetrating radiation and its accompanying secondary radiation produced in the gas. (In this proof the radiation was assumed to have a penetration comparable with that ordinarily assigned to a cosmical-penetrating radiation.) In view of the preceding conclusion, the fact that an upper limit is obtained for the ionization at the higher pressures indicates that no appreciable part of the ionization at atmospheric pressure is produced by the direct or indirect action on the gas itself of a radiation of a highly penetrating type. Most if not all of the ionization then appears to be due to the direct action of a radiation of a penetration low compared with that usually attributed to the cosmical radiation. It is probable that this is radiation of the corpuscular type emitted from the walls of the vessel by impurities or by the primary radiation. The ionization pressure curves indicate that the radiation is completely absorbed at pressures above 47 atmospheres.

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[1] Bulletin of the National Research Council, No. 17, pp. 65–73, 1922.

In the previous experiments performed over the Mississippi River in 1919 with a range of pressure from zero to 22 atmospheres, the values obtained for Δq on May 16 and May 17 were 1.55 and 1.58 ions per c.c. per second per atmosphere increase respectively. Since in these experiments the radiation from the soil was absorbed by the layer of water, it is apparent that in the present experiments (where lower values for Δq were obtained) the walls of the laboratory building served to screen away more of the shorter range radiation in the atmosphere.

Even the average value for Δq, 1.25 pairs of ions per c.c. per second, obtained from the portion *AB* of the curves of Figures I., II., III., and IV. (Table II.), is lower than the values at atmospheric pressure that have been given by other observers. McLennan and Murray found that 2.6 pairs of ions per c.c. per second were produced at atmospheric pressure in a vessel of ice.[1] Up to the present time this appears to be the lowest value obtained by direct measurement, but it may be noted here that Gockel estimated an approximate value as low as 1.66 for the number of pairs of ions produced per c.c. per second at atmospheric pressure.[2] McLennan and Murray seem to favor the view that this ionization is due to radioactive impurities in the material of the ionization chamber. In the light of present experiments it would be of interest to compare the penetration of the radiation given off by more common radioactive substances. Sodium and potassium are, of course, common impurities. While there have been experiments by N. R. Campbell indicating that potassium is radioactive, there seems to be no definite information as to any radiation which may be emitted.

"RADIUM" CURVES AND GENERAL DEDUCTIONS.

In the writer's work for the sake of comparison it seemed best to repeat the ionization pressure experiments with radium-bromide placed 8 feet from the inoization spheres. The values thus obtained are given in Curves V. and VI. A two-milligram sample of radium-bromide enclosed in a lead box (walls of which were 1.5 cm. in thickness) was used for these experiments, but when the values for Fig. 6 were obtained, the radium bromide was shielded by additional plates of lead. It is evident from the graphs that the ionization values for the curve of Fig. 5 are greater than those for the same pressures in the curve of Fig. 6, which of course represents ionization due to the harder type of radiation.

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[1] Phil. Mag., 30, p. 428, 1915.

[2] Phys. Zeit., 16, pp. 345–352, 1915.

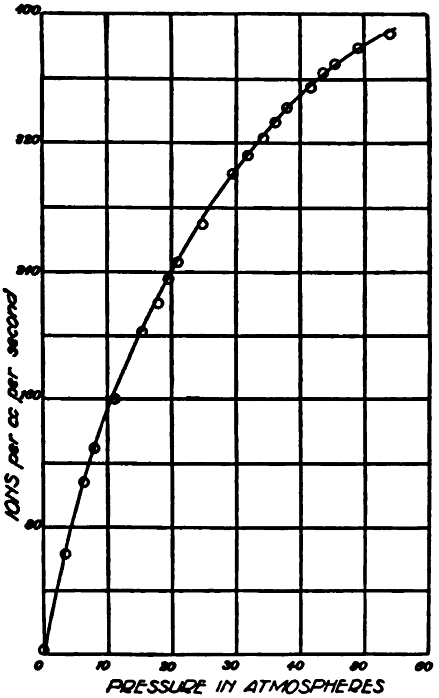

Fig. 5.

Ionization due to the gamma rays of radium.

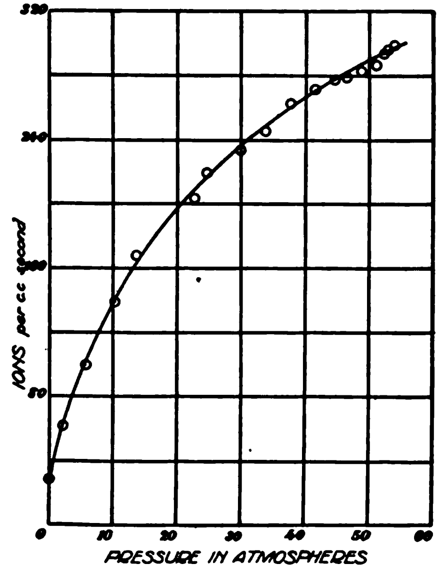

Fig. 6.

Ionization due to the gamma rays of radium. The shielding of the radium bromide used was greater for these observations than for those of Fig. 5.

It is apparent that the upper limit of the ionization shown by the "residual ionization" curves is not to be found in the "radium" curves.

So far as the residual ionization at atmospheric pressure is concerned, it is obvious that the ionization due to the action of the penetrating radiation on the gas itself is practically immeasurable. It would seem than that the residual ionization must be attributed for the most part either to radiation emitted by impurities in the walls of the vessel or to secondary radiation from these walls.

This experimental work was carried on during the summer of 1920 in

the University of Minnesota. I am indebted to Professor F. B. Rowley, of the experimental engineering laboratories, for the calibration of the pressure gauge used in these experiments, and to the department of physics for the use of the laboratory facilities. I wish to express my most sincere thanks to Professor W. F. G. Swann, who has suggested this problem and given me much helpful advice throughout the course of this work.

Physical Laboratory,
University of Minnesota,
December, 1921.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

MINUTES OF THE SALT LAKE CITY MEETING, JUNE 23, 1922.

THE 115th regular meeting of the American Physical Society was held at the University of Utah at 9:30, June 23, 1922, in connection with the annual meeting of the Pacific Division of the American Association for the Advancement of Science.

Professor Orin Tugman presided.

About fifty members and friends were in attendance.

The following papers were presented, four being read by title:

1. Symmetry of Emergent and Incident Photoelectronic Velocities. ROBERT J. PIERSOL.
2. The Electrical Conductivity of Metallic Films when Exposed to Ultra-Violet Light. ORIN TUGMAN.
3. The Capillary Potential Function and its Relation to Irrigation Practice. WILLARD GARDNER, O. W. ISRAELSON, N. E. EDLEFSEN, and HARRY CLYDE.
4. A New Method of Mechanical Analysis of Soils. D. S. JENNINGS, M. D. THOMAS, and WILLARD GARDNER.
5. Test of Coagulative Power by Means of the Centrifuge. E. F. BURTON and J. E. CURRIE.
6. Energy Distribution in X-Ray Spectra. PAUL KIRKPATRICK.
7. The Limiting Frequency of the Photoelectric Effect. RICHARD HAMER.
8. The Absorption of Light by Sodium Vapor. GEORGE R. HARRISON.
9. The Relative Deposition of Radium and Barium Salts as a Function of Temperature and Acidity. W. B. PIETENPOL.
10. Breaking an Inductive Circuit. W. P. BOYNTON.
11. Radii of the Atoms of the Alkali Metal Vapors. S. H. ANDERSON.
12. The Hygroscopicity of Soils. M. D. THOMAS.
13. A General Method of Determining the Adiabatic Invariants of Mechanical Systems. V. F. LENZEN.
14. An Extension of the Principle of the Diffraction Evolute and Some of its Structural Detail. G. G. BECKNELL and JOHN COULSON.

The abstracts of the papers in the above program, with corresponding numbers, are given on the following pages.

E. P. LEWIS,
Local Secretary for the Pacific Coast.

1. Symmetry of Emergent and Incident Photoelectronic Velocities.

By Robert James Piersol.

When ultra-violet light from a Cooper-Hewitt lamp strikes a platinum film sputtered on quartz, results show that the percentage of asymmetry between the emergent and incident velocity of photo-electrons decreases directly with decrease in reflected light. These results are checked with visible mono-chromatic light, using an argon-filled Kunz photo-electric cell of which the inner lining is potassium.

A guard ring type of photo-electric cell is so constructed as to eliminate any light from being reflected to the receiving gauze. The film may be rotated through 360 degrees. Using mono-chromatic light on the platinum film the photoelectronic velocity remains constant in emergent and incident positions as well as when rotated by ten-degree intervals throughout the circle.

These results are in accordance with theoretical considerations of the quantum theory which lead to the conclusion that photo-electrons are emitted from the parent atoms, due to the storing up of definite quanta of energy, thereby imparting to the photoelectrons a velocity independent of the direction of the exciting light.

Department of Physics,
University of Pittsburgh.

2. The Electrical Conductivity of Metallic Films when Exposed to Ultraviolet Light.

By Orin Tugman.

Metallic films formed on mica by cathode deposition were made of such thickness that their conductivity could be determined by measuring the time of charging a quadrant electrometer through them. The films were placed in a vacuum and exposed to the light so as to reduce the conductivity due to ionization by the light. Later this source of error was found not to be a serious factor and the films were exposed to the light in the air.

When the electrometer was charged positively through the film with the light on, the time of charging was less than when the light was off, and when the electrometer was charged negatively under the same conditions the time of charging was greater depending on the potential applied. This result may be explained by the photo-electric effect.

The conductivity of the film decreased with time when the current was on. A reversal of the current showed the film to have a greater conductivity which decreased with time until the current was reversed again. Data showing this result and the time of charging the electrometer positively and negatively with light on the film were obtained.

University of Utah.

3. THE CAPILLARY POTENTIAL FUNCTION AND ITS RELATION TO IRRIGATION PRACTICE.

BY WILLARD GARDNER, O. W. ISRAELSEN, N. E. EDLEFSEN, AND HARRY CLYDE.

THIS paper is an attempt to apply quantitative methods to the solution of physical problems encountered in irrigation practice.

It is shown that there exists a capillary potential increasing continuously with the moisture content over a wide range. For the soil at the experimental farm the following equation is found to fit experimental data:

$$(\psi + 145)(\rho - 0.173) = -42.6.$$

ψ is the capillary potential measured in gram-centimeters, the origin taken at the saturation point. ρ is the moisture content in grams per c.c. From this equation, with experimental data and theoretical equations previously published, it is shown that an allowance of approximately 0.25 cm. of water per day should be made for loss into the deeper soil.

The apparatus used consists of a porous cup closed with a water-tight joint and connected through a tall tube to an exhaust pump. The cup is surrounded by a thin layer of soil in an outer vessel and atmospheric pressure maintained on the soil side. The pressure is then reduced on the water side and measured, and by means of the glass tube the amount of water in the soil is determined.

UTAH AGRICULTURAL EXPERIMENT STATION.

4. A NEW METHOD OF MECHANICAL ANALYSIS OF SOILS.

BY D. S. JENNINGS, M. D. THOMAS AND WILLARD GARDNER.

THIS method consists in shaking a deflocculated soil suspension in a cylindrical vessel and determining the concentration at measured distances below the surface as it changes with the time. It involves the assumption that the particles fall as individuals at a constant rate.

Since the suspension density q at a point at distance h beneath the surface is due to the presence of a large number of different sized particles and the decrease in this density with the time results from the disappearance, one by one, of the separate species, the concentration of any species will remain constant at this point until those particles of this species originally at the surface have fallen through the distance h.

The "equivalent" radius r of the particles of the species vanishing at point h at time t is obtained from Stokes's equation and the experimental curve made to represent q as a function of r. Then, from the relation,

$$q = k\int_0^r w dr$$

or

$$dq/dr = kw$$

(where w is the weight of soil corresponding to r and k is a proportionality factor) the value of w for any value of r may be obtained.

Analysis of two soils by this method and a standard method gave good agreement.

Utah Agricultural Experiment Station.

5. Test of Coagulative Power by Means of the Centrifuge.

By E. F. Burton and J. E. Currie.

Quantitative tests have been made on the amount of coagulum precipitated from colloidal solutions by additions of electrolytes when the samples have been centrifuged for a few minutes. The solution used was arsenious sulphide and the coagulant aluminium sulphate. Indications of complete coagulation are given in a few minutes, the results of which agree with the effects on the same samples when left standing for days under ordinary settling. This not only gives a quick method for testing coagulation, but there are indications of a definite gradation in the size of the arsenic sulphide particles due to the added electrolyte—a result which is well known from optical determinations on gold solutions.

Department of Physics,
University of Toronto, Canada.

6. Energy Distribution in Continuous X-ray Spectra.

By Paul Kirkpatrick.

Spectrum curves were corrected for various distorting influences. Superposed orders at the larger crystal angles were separated by a study of the intensity-potential curves with fixed crystal setting. These results checked well with results from an absorption study of the complex reflections.

Energy was assumed proportional to ionization produced by complete absorption in methyl iodide vapor. Degree of completeness actually realized was determined for different wave lengths by direct measurements upon a volume of the gas. Correction was made for varying reflectivity of the rock-salt crystal by the reflection equation used by W. L. Bragg and co-workers and the values of F as measured by them.[1] Absorptions by the wall of the Coolidge tube were determined from actual observations upon the tube itself.

The corrected curves should give the energy distribution at the emitting center save for absorption in the tungsten target. The final curve differs from the original in that the maximum is displaced toward longer wave-lengths and intensities of long wave-lengths are increased relatively many fold. The curves do not show good agreement with the theoretical energy distributions of Davis or of Behnken.

The x-ray tube was operated from a transformer but constant potential conditions to within one per cent. were simulated by the use of a synchronous shutter. Curves obtained without the shutter show, when corrected, no maximum within the observable range.

University of California.

[1] Phil. Mag., Mar., July, 1921.

7. THE LIMITING FREQUENCY OF THE PHOTO-ELECTRIC EFFECT.

BY RICHARD HAMER.

A MIRROR spectrograph was used as a monochromator. The prism was of fluorite and the concave mirror covered with a cathodic deposit of platinum. Light passing at the angle of minimum deviation entered the photo-electric cell through a narrow slit and fell on electrodes of the metals investigated, which were connected with a sensitive string electrometer.

The source was a carbon arc with cored carbons saturated with solutions of iron and other metals, giving a nearly continuous spectrum.

The metals were thoroughly cleaned with sandpaper and the cell was exhausted to a pressure of about 0.006 mm. The wave-length at which there was a sudden increase in the saturation current was taken as the limiting wave-length. Errors due to scattered light were eliminated as far as possible by screens.

The following values were determined:

Silver	λ3391 ± 60
Platinum	2782 ± 35
Aluminum	3596 ± 100
Cadmium	3130 ± 50
Tin	3185 ± 55
Lead	2980 ± 50
Iron	2870 ± 40
Nickel	3050 ± 50
Tungsten	2615 ± 30
Copper	2665 ± 30
Zinc	3426 ± 75
Brass	3426 ± 75 (with indications of increase at 2665)
CuO	2665 ± 50
Methyl Violet	2585 ± 30

UNIVERSITY OF CALIFORNIA.

8. THE ABSORPTION OF LIGHT BY SODIUM VAPOR.

BY GEORGE R. HARRISON.

THE absorption of light by sodium vapor in the visible and near ultra-violet has been studied, particularly in relation to temperature, vapor saturation. and hydrogen pressure. Light from a Cd spark or electrically exploded wires was used as a source.

It was found that the continuous absorption at the limit of the principal series is intense over only a very limited range of wave-lengths, and does not extend undiminished to the extreme ultra-violet, as has been supposed. It apparently decreases rapidly with decreasing wave-length, in a manner similar to the analogous case with x-rays, although the exact function has not yet been determined.

The continuous absorption follows the line absorption very closely in changing in intensity with vapor density, so that they appear to originate in the same entity. It is unaffected by hydrogen pressure within the range 2 mm. to 400 mm.

Pictures were obtained with unsaturated vapor showing 25 members of the line spectrum together with the continuous absorption, while the band absorption was entirely absent except for a trace around the D-lines. This indicates that the band absorption may originate in a loose molecular aggregate which is broken up on superheating. Evidence from Hackspill's vapor density determinations seems to show that such may exist.

Stanford University.

9. The Relative Deposition of Radium and Barium Salts as a Function of Temperature and Acidity.

By W. B. Pietenpol.

In the commercial refining of radium the radium salts are commonly purified by fractional crystallization of a radium-barium solution. In cooling from boiling to room temperature a percentage of radium largely in excess of that of the barium is deposited with the crystals.

Under similar conditions of cooling the relative amounts of radium and barium deposited have been determined at different temperatures throughout the cooling process and curves plotted. Determinations of the above nature have been made with radium-barium solutions of different acidity and the variation in the form of the curves shown.

The first crystals formed in the solution contain a larger percentage of radium than succeeding crystals. It is pointed out that the efficiency of the refining process may be increased by separating liquor and crystals at a point above room temperature. In this way the factor of enrichment is increased in addition to a saving in time.

The rate at which the solution cools is a factor in the relative amounts of radium and barium deposited. With rapid cooling a smaller percentage of radium is adsorbed than with slow cooling. Work on the nature of the adsorption of radium by barium is in progress.

University of Colorado.

10. Breaking an Inductive Circuit.

By W. P. Boynton.

When a switch is opened in an inductive circuit carrying an electrical currents the current decreases gradually to its final zero value during the persistence of the arc at the switch points. Obviously the resistance of the circuit i, increasing during that time from its initial finite value to infinity, and making this change continuously. This change of resistance can be represented as a first approximation by the form[1] previously used by the author for the resistance of a quenched spark,

$$R = \frac{R_1}{1 - at}.$$

For an approximate solution we may disregard, from the time of opening of the switch, both the e.m.f. acting in the circuit and the counter e.m.f. of ionization of the arc. The differential equation of the circuit then becomes

$$O = \frac{R_0}{1 - at} I + L \frac{dI}{dt},$$

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[1] Phys. Rev. (2), 4, pp. 511–514.

in which separation of the variables gives the solution

$$0 = -\frac{R_0}{a} ln(1 - at) + L ln \frac{I}{I_0}$$

or

$$I = I_0(1 - at)^{R_0/aL}.$$

In the particular case where $R_0/aL = 1$ or $1/a = L/R_0$, that is, when the time of persistence of the arc is equal to the relaxation time of the circuit with its initial resistance, the current falls off as a linear function of the time. For other values of the exponent the curve bows up or down, passing however through the same two end-points.

UNIVERSITY OF OREGON.

11. RADII OF THE ATOMS OF THE ALKALI METAL VAPORS.

BY S. H. ANDERSON.

THE radii of the valency electrons of the alkali metal vapors have been computed on the basis of the following assumptions: (1) that the ionizing potential is one half the potential of a point on the orbit of the valency electron; (2) that the distribution of the electrons in the kernel of the atom is that suggested by Bury[1] and Bohr.[2]

For the lithium atom the distance of the electrons in the kernel from the center of the nucleus is that computed by Langmuir[3] for the helium atom. For the other alkali metals the dimensions of the inner shells of electrons are computed from Bragg's[4] values of the elementary crystals of the alkaline halides.

The values obtained for the radii of the valency electrons are as follows:

Lithium	1.379 × 10^{-8} cm.
Sodium	1.80 "
Potassium	2.21 "
Rubidium	2.45 "
Caesium	2.695 "

If these values are plotted against the integral numbers 2, 3, 4, 5, and 6, the points are uniformly distributed about a straight line, showing that in passing from one metal to the next higher in the periodic table an extra electron shell is added to the atomic structure and that the shells are spaced evenly. This relationship is in better agreement with Bury's modification of Langmuir's theory than with the latter's original theory of atomic structure.

UNIVERSITY OF WASHINGTON,
SEATTLE, WASH.

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[1] Bury, Journal Amer. Chem. Soc., Vol. 43, 1921, p. 1602.

[2] Bohr, Nature, Vol. 107, 1921, p. 105.

[3] Langmuir, PHYS. REV., Vol. 17, 1921, p. 339.

[4] Bragg, Phil. Mag., Vol. 40, 1920, p. 169.

12. The Hygroscopicity of Soil.

By M. D. Thomas.

Vapor-pressure measurements at 25 degrees C. have been made by the air-saturation method, on a group of soils of widely differing textures. The moisture content of each soil was varied so that the pressure data ranged from 10 to 97 per cent. of the vapor pressure of water.

The ratios of the moisture percentages of the soils at the same vapor pressure are nearly constant over this range of pressures. Heating the soil at 100° C. increases the vapor pressure at the same moisture content, while wetting and air-drying reverses this action. Each curve of the series is shifted proportionately by this process. The mechanical analyses also indicate that heating the soil makes the texture coarser.

Size-frequency distribution curves for these soils have been worked out, the observations being taken to 0.04 μ radius. The total surface per gram, calculated from these data, agrees only qualitatively with the ratios of the vapor-pressure curves. The total surface of the particles larger than 0.25 μ, disregarding the smaller material, give ratios in good agreement with the vapor-pressure measurements. The data seem to bear out the idea of colloid-coated particles.

Utah Agricultural College.

13. A General Method of Determining the Adiabatic Invariants of Mechanical Systems.

By V. F. Lenzen.

P. Ehrenfest has introduced into the quantum theory the consideration of reversible adiabatic transformations of mechanical systems. Quantities which remain unchanged during such transformations are called *adiabatic invariants.* In his fundamental article Ehrenfest states that it would be desirable to develop a systematic method of finding adiabatic invariants for systems as generally as possible. This paper is a contribution toward that end. The problem is attacked with the aid of the theory of continuous groups. The method consists in determining the equations by means of which a given state of motion of the system may be transformed into an adiabatically related one. The infinitesimal transformation Uf is derived and use is made of the theorem that a function is invariant under the group if $Uf = 0$. The method is illustrated by application to the problem of the simple pendulum discussed in Sommerfeld, Atombau, 3d ed. The variables used are the average kinetic energy $\overline{T}$ and the frequency ν. The change in length of the pendulum is denoted by a. The transformation equations are

$$\overline{T}_1 = \sqrt{\frac{g}{g + 4\pi^2\nu^2 a}}\,\overline{T},$$

$$\nu_1 = \sqrt{\frac{g}{g + 4\pi^2\nu^2 a}}\,\nu;$$

$$Uf = -\frac{2\pi^2\nu^2}{g}\left[\overline{T}\frac{\partial f}{\partial \overline{T}} + \nu\frac{\partial f}{\partial \nu}\right] = 0$$

is the equation which $f(\overline{T}, \nu)$ must satisfy in order to be invariant under the transformation.

DEPARTMENT OF PHYSICS,
UNIVERSITY OF CALIFORNIA.

14. AN EXTENSION OF THE PRINCIPLE OF THE DIFFRACTION EVOLUTE, AND SOME OF ITS STRUCTURAL DETAIL.

BY G. G. BECKNELL AND JOHN COULSON.

IT has been shown in a paper read before this Society[1] that the predominant figure in the diffraction patterns produced by comparatively large discs and elliptical plates when illuminated by a point source of light is *the evolute of the corresponding geometrical shadow.*

Accurate hyperbolic and parabolic plates are found to produce diffraction figures conforming to the principle just mentioned.

A ¾-inch auger bit of about 1-inch pitch ground to the form of a truncated cone produces a well-defined Arago spot at the center of the geometrical shadow when the point source of light is at the apex of the cone; but does not do so if the point source is not fairly close to this position. In the first case the shadow is strictly circular. The diffraction pattern and geometrical shadow are identical with those produced by a thin disc, but here the explanation in terms of the Fresnel zones is certainly not applicable.

The experiments described here and in the preceding paper point to the following general principle:

Any particular form of geometrical shadow is always associated with the same diffraction pattern whatever be the diffracting object.

A study of the structural detail of the diffraction patterns produced by discs and elliptical plates has been made. Photographs taken at distances of 20 to 30 meters from the diffracting objects reveal four series of alternate dark and bright bands each set of which is parallel to a quadrant of the diffraction evolute. The evolute itself is formed by the extremities of these bands, and consequently is not a continuous bright line.

UNIVERSITY OF PITTSBURGH.

[1] Washington meeting, 1922.

Second Series *September, 1922* *Vol. XX., No. 3*

THE

PHYSICAL REVIEW.

THE OPTICAL CONSTANTS OF SODIUM-POTASSIUM ALLOYS.

By Raymond Morgan.

Synopsis.

The optical constants of sodium-potassium alloys were investigated for an entire alloy series by the polarimetric method. Bright metallic surfaces were obtained by filling glass cells with the molten metal in a vacuum. Excepting sodium, all the specimens were observed in the liquid form. In the region near the composition corresponding to NaK the refractivity-concentration curve has a maximum value of 0.137 and the absorptive index-concentration curve has a minimum value of 12.5. *The effect of change in temperature* was studied for some of the mirrors. The solid alloy containing 83 per cent. Na showed a change in the optical constants with a change in temperature, but no change was found for the liquid alloy containing 26 per cent Na. It could not be definitely determined whether the change observed for the solid alloy was due to a change in the optical constants or was due to a possible surface effect resulting from the metal expanding and making better contact with the glass.

THE optical properties of alkali metals have been studied by a number of investigators[1] but as yet no study has been made of the alloys of these metals. Some work has been done on the determination of the optical constants of the alloys of the less oxidizable metals. Binary mixtures of Ag-Te, Ag-Sn, Cd-Hg, Cu-Sn, Cu-Zn and Cu-Ni were studied by Bernouilli.[2] An investigation of the entire alloy series was made for Cu-Ni, Fe-Mn, Ni-Fe, Al-Cu and Cu-Fe by Littleton.[3] Binary alloys of silver with copper and platinum have been studied by Oppitz.[4] Recently Kent[5] has studied bismuth, cadmium, tin, lead, and binary alloys of these. His observations were made on the metals in the molten state. In continuation of the work this paper gives the results of a determination of the optical constants of sodium-potassium alloys by the polarimetric method.

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[1] Drude, Ann. d. Phys., p. 159, 64, 1898. R. W. and R. C. Duncan, Phys. Rev., 36, 294, 1913. Meese, Gottingen Nachr. Math. Phys. Klasse. Nathanson, (1) Astro. Phys., 44, 137, 1916; (2) Phys. Rev., 11, 227, 1918. Frehafer, Phys. Rev., 15, 110, 1920.

[2] Bernouilli, Zeitschr. f. Elektrochemie, 15, 647, 1909.

[3] Littleton, Phys. Rev., 28, 306, 1912; 33, 453, 1912.

[4] Oppitz, Phys. Rev., 10, 156, 1917.

[5] Kent, Phys. Rev., 14, 459, 1919.

The Preparation of the Surface.

Bright metallic surfaces were obtained by filling glass cells (Fig. 1) with the molten metal in a vacuum.[1] Each cell consisted of a cylindrical glass ring 12 mm. in diameter and 8 mm. wide. On the side of the ring was sealed a tube *E* through which the cell was filled. A fine tube *F* sealed inside of *E* helped to prevent metallic oxides from getting into the cell. Plane glass plates were fastened with rock cement on the carefully ground sides of the ring. Only a thin coat of the cement was used and this after being baked at about 140° C. for forty hours was coated with Whiz black engine enamel and again baked.

The melting point curve[2] (Fig. 7) for sodium-potassium alloys shows that at room temperature some of the alloys are solids and some are liquids. At present only two investigations have been made upon the effect of the change of state on the optical constants of a metal and the results of these are not in agreement. Data given by Kent[3] for bismuth, lead, cadmium and tin show a difference in the optical properties for the liquid and solid states of these metals. On the other hand it was found by J. J. Haak and K. Sissingh[4] that liquid and solid mercury behave optically in the same way.

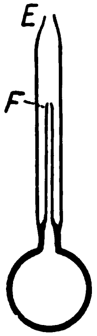

Fig. 1.

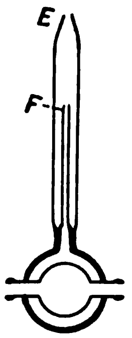

Fig. 2.

In the case of the solid alloys of sodium and potassium special glass cells (Fig. 2) were constructed by means of which observations could be made on the specimens in both the solid and liquid forms. These cells were made with an internal bulb to which outlet tubes were sealed through the sides of the rim. By passing hot water or steam through the bulb on the interior of the cell the solid metals could be melted. By this method any considerable difference between the results for the mirrors in both the solid and liquid states could easily be detected.

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[1] This method is, in general, the same as used by R. W. and R. C. Duncan in obtaining bright surfaces of sodium and potassium.—PHYS. REV., 36. 294. 1913.

[2] Kurnakow and Puschin, Z. Anorg. Chem., 30, 109, 1902.

[3] Kent, *loc. cit.*

[4] J. J. Haak and K. Sissingh, K. Akad. Amsterdam, 5, 692, 1919.

The cells were filled by use of the apparatus shown in Fig. 3. The metal placed in *C* was melted by means of an oil bath. Upon turning *C* in the ground class joint *a* the molten metal would run to the bottom of *A*. The pouring device had the great advantage of getting rid of much of the oxide. The cell was lowered by means of the windlass *B* until the end of the filling tube *E* was well under the surface of the metal. The air now being let in at *D* the metal was pushed into the cell. After the whole apparatus had been allowed to cool, the mirror was taken out and the end of the tube *E* was closed with paraffin. The metal remaining in *C* and *A* was removed with alcohol.

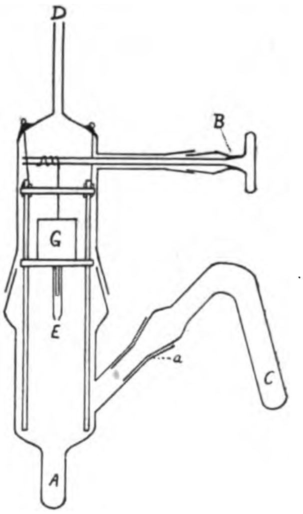

Fig. 3.

Before the tube was lowered into the metal and with the evacuating pumps in operation, the plane glass plates on the sides of the cell were heated in order to drive off occluded gases. The heating was effected by placing the cell in the grid *G* on the sides of which were pieces of mica wound with fine platinum wire. By sending an electric current through the wire it was heated until it was bright red. With the wire thus heated the pumping was continued for about forty-five minutes. After heat treatment the grid was allowed to cool down to a temperature slightly higher than the melting point of the alloy.

The quantities of sodium and potassium to make up an alloy were prepared by cutting off the heavy coats of oxide under paraffin oil. After sponging off the excess oil from the pieces they were placed in known amounts of paraffin oil and weighed. The pieces were then rinsed in gasoline and quickly transferred to *C*. Chemical analyses made of two alloys checked the percentages obtained by the above method to one per cent.[1]

Much difficulty was experienced in obtaining suitable mirrors, there being many opportunities for failure in the process of preparing the cells and filling them with metal. In all over thirty-five mirrors were made to obtain the ten that were used for the observations. The greatest difficulties were caused by the occurrence of thin oxide films on the surface and by the metal not making good contact with the glass. Excepting the potassium mirror the ones used for investigation were without fault so far as the eye could tell.

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[1] The writer desires to express his thanks to Mr. R. W. Pfanstiel for assistance in making the chemical analyses.

Evacuation was accomplished by means of a Gaede molecular pump supported by a Gaede mercury pump in series with a single stage oil pump.

OPTICAL METHOD.

As Drude's method of investigating the optical constants of metals was used throughout this work, it was necessary to observe the values of Δ the phase difference and ψ the azimuth of restored polarization. These were determined by means of a Soleil-Babinet compensator and two nicols mounted on a spectrometer. The nicol used as an analyzer was of the form of the Zehnder half-shadow polarimeter.[1] The settings of the nicol and compensator were made by removing the eye-piece of the telescope and looking directly at the nicol through a small hole placed at the focus of the objective lens in the telescope. A circular field of light was viewed in making the settings. The position of extinction of the analyzing nicol was determined by finding two half-shadow equality positions one on each side of the extinction position.

A Cooper-Hewitt glass tube mercury arc was used as the source of light. The light was separated into its component colors by means of a constant deviation monochromator. The green line 5461 Å. was used. The eye-piece of the monochromator being removed, the beam of green light was allowed to fall on the slit *s* (Fig. 4) of the collimator of the

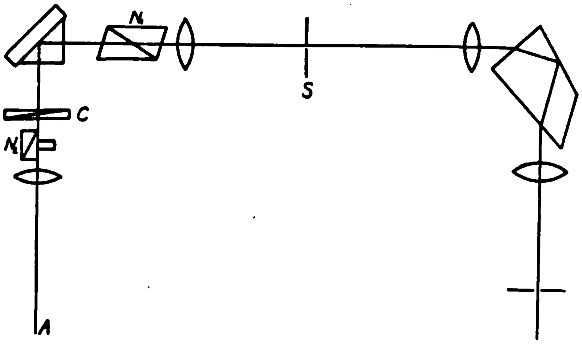

Fig. 4.

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[1] Zehnder, Ann. d. Phys., 26 pp. 985, 1908.

spectrometer. The light after passing through the collimator was polarized by the nicol N_1 at an azimuth of 45°.

The mirrors were mounted against the hypotenuse side of a right-angled prism. Either cedar oil or Canada Balsam was placed between the mirror and the prism. One leg of the prism being set normally to the incident light, the light would accordingly strike the metal surface at an angle of 45° and after reflection would pass out normally through the other leg of the prism. The light then passed through the compensator C and the analyzing nicol N_2 and out through the telescope tube A.

The prism used throughout the work was tested for strains by measuring the phase change Δ for internal reflection from the hypotenuse side. The experimental value agreed very closely with the theoretical value as calculated by Drude's equation. Several prisms were examined before one was found that did not give a difference in the two values of Δ.

In the following table is given a summary of the data taken in a particular case for calculating 2ψ. In determining the position of extinction, from 5 to 10 settings of the analyzer for half-shadow equality were made on each side of the extinction position. Accordingly, from 80 to 160 settings of the analyzer were made to obtain one value of 2ψ. The determinations of the phase difference indicated by the compensator are obvious.

TABLE I.

Position of Polarizer.	10° 54′.	190° 54′.	100° 54′.	280° 54′.
Position of analyzer	213° 64.9′ 33° 56.4′	213° 62.2′ 33° 55.4′	305° 17.8′ 125° 18.1′	315° 15.6′ 125° 16.7′
Mean	213° 59.7′		125° 17.0′	
2ψ	88° 42.7′			

RESULTS.

The values of the optical constants were obtained by substitution in the approximative form of Drude's equations as used by R. W. and R. C. Duncan.[1]

The results of the measurements upon a complete series of alloys are given in Table II. With the exception of sodium it is believed that the values obtained for n (index of refraction) and k (index of absorption) are within 10 per cent. of the actual values. The reflecting power R

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[1] R. W. and R. C. Duncan, loc. cit.

was calculated from the mean value of *n* and *k*. The specimens were all in the liquid state excepting sodium and in one case potassium. From other data subsequently given, it is probable that there is not a wide variation between the constants for the solid and liquid states. The index of refraction from air to metal is that given in every case.

The results are shown graphically in Figs. 5 and 6. No attempt was made to determine the detailed form of the curves as this would have required measurements on a very large number of mirrors. The curves show, however, that in the region near the eutectic points the index of refraction reaches a maximum and the index of absorption becomes a minimum. The variations of the optical properties of the alloys with the concentration are therefore in the opposite sense from

Table II.

Mirror No.	Per Cent. of Potassium by Weight.	Atomic Per Cent. of Potassium.	2ψ.	Δ.	n.	k.	Mean n.	Mean k.	R.
1	0	0	89° 20.9′	131.3°	.041	52.5	.047	47.3	96.9
2			89° 14.2′	131.4°	.047	46.1			
3			89° 18.3′	133.8°	.047	48.7			
3			89° 11.6′	132.7°	.053	42.1			
1	17.3	11.0	88° 42.7′	132.4°	.083	26.4	.081	27.2	94.6
1			88° 47.0′	132.5°	.079	28.0			
1	36.2	25.1	88° 9.5′	126.4°	.100	18.5	.100	18.5	91.4
1	45.0	32.5	87° 58.0′	125.5°	.108	16.9	.108	16.8	90.4
1			87° 58.2′	125.6°	.108	16.8			
1	55	41.8	87° 51.3′	125.1°	.113	15.9	.115	15.6	89.7
1			87° 47.0′	125.5°	.117	15.4			
1	66	53.3	87° 23.0′	124.5°	.135	12.9	.137	12.5	87.0
2			87° 14.3′	122.7°	.137	12.1			
2			87° 14.3′	123.3°	.139	12.5			
1	74.2	62.7	87° 25.2′	122.7°	.128	13.0	.124	12.8	86.9
2			87° 19.4′	122.5°	.132	12.5			
1			87° 27.4′	119.8°	.119	12.9			
1			87° 27.5′	119.9°	.118	12.9			
	84.3	76	88° 7.5′	120.3°	.088	17.6	.088	17.6	90.2
1	100	100	88° 39.0′	119.5°	.062	19.3	.060	21.5	91.4
1			88° 40.8′	115.8°	.057	23.6			

those found by Oppitz[1] for the optical constants of silver-copper alloys. In the case of the alloy series of Al-Cu, Cu-Ni, and Cu-Fe, Littleton[2] found that the indices of refraction increased to a value higher than that of either component forming the series and the index of absorption became a minimum at about the same concentration. This is similar to the results for sodium-potassium alloys.

Temperature Effects.

In some cases when the mirrors were heated in order to convert the metal into the liquid state, considerable changes of the optical constants were noted with changes in the temperature. A number of observations were accordingly made in order to determine more closely the effect of changing the temperature upon the optical constants.

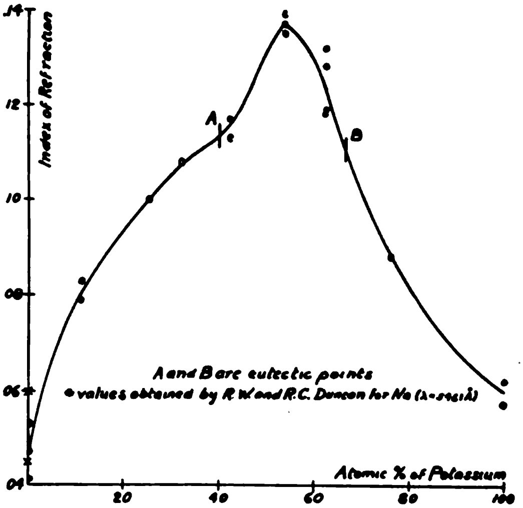

Fig. 5.

82.7 per cent. sodium and 17.3 per cent. potassium.—The results for this alloy are given in Table III. and a graphical representation of the probable variation of the refractive index with temperature is given in Fig. 8. The change in the optical constants in raising the temperature from 75° C. to 100° C. was less than the experimental error.

Sodium.—In making the measurements on the sodium mirror the field as viewed in setting the analyzer and compensator became distorted, a light circular band appearing on one side of the field. The

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[1] Oppitz, loc. cit.

[2] Littleton, loc. cit.

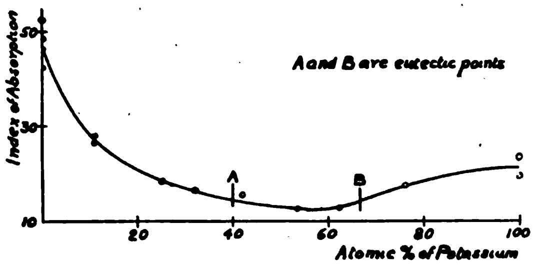

Fig. 6.

distortion was first noticeable at a temperature of about 60° C. and was quite marked at 100° C. It was also noted that the two positions of the analyzer for one setting of the polarizer lacked as much as 40′ of being 180° apart. Fairly consistent results showing a change in the optical constants were obtained for temperatures of 26°, 60° and 100° C., but they are not considered as reliable.

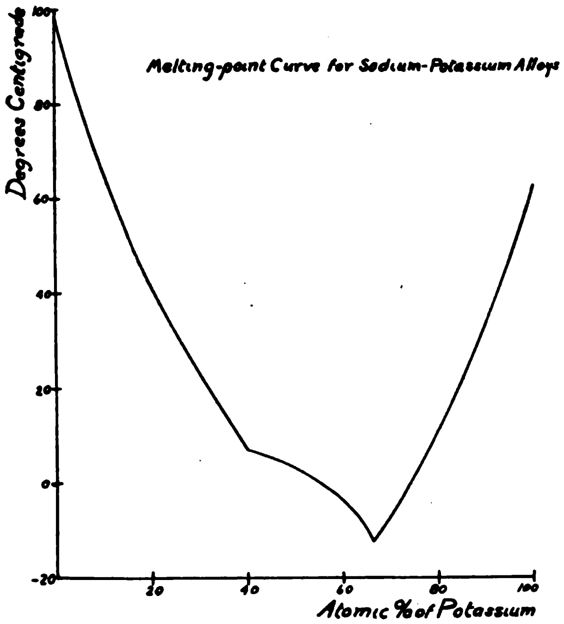

Fig. 7.

It is most probable that the strains present in the sodium mirror were produced in the cover glasses by the unequal expansion of the cylindrical wall of the cell. The small ring with the three tubes sealed to it was a very complicated piece of glass blowing and would be likely to be under such high tension that when heated it would expand unequally and produce strain in the cover glasses. A few empty cells were examined for such strains. The method of examination consisted in mounting the right-angled prism with its hypotenuse side against an empty cell so that the light was totally reflected from the back surface of the cover glass, and measuring the phase change Δ when water at 15° C. and later steam at 100° C. were passed through the bulb in the cell. The greatest variation in Δ found for the two temperatures was a little less than two degrees. In this case the field viewed in making the analyzer and polarizer settings was slightly distorted. The cell that contained the alloy, 82.7 per cent. sodium and 17.3 per cent. potassium, showed no variation at all.

Potassium.—Table IV. In order to make the observations on potassium, the mirror had to be heated so as to free the surface of the irregularities due to the contraction of the metal from the glass. At a temperature of 54° C. the surface irregularities were found to disappear and the field as viewed in making the settings of the analyzer and compensator became of uniform intensity.

25.8 per cent. sodium and 74.2 per cent. potassium.—Table V. As this mirror did not contain a heating bulb the heating was effected by means of fine platinum wire wound on mica. Sufficiently accurate values of the temperatures were obtained by taking a mercury mirror of the same size and shape as the above mirror, mounting it under exactly the same conditions and by means of a small mercury thermometer inserted in the mirror noting the temperature for different values of the current. The variations in the values of n and k are within the limits of experimental error.

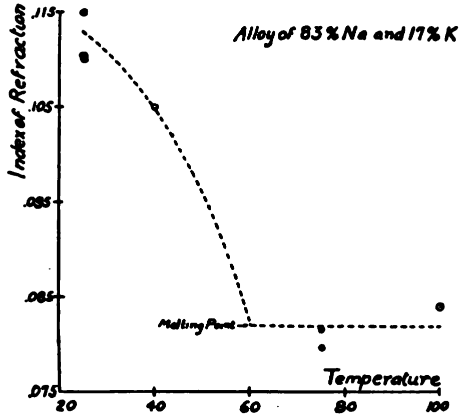

Fig. 8.

TABLE III.

82.7 Per Cent. Sodium and 17.3 Per Cent. Potassium.

Date of Observation.	Temperature.	2ψ.	Δ.	n.	k.
11/22/21	Room 27°	88° 4.9′	130°	.115	17.9
11/24/21	75°	88° 42.7′	132.4°	.083	26.4
11/25/21	Room (24°)	88° 1.1′	128.7°	.115	17.3
11/27/21	40°	88° 15.2′	130.3°	.105	19.6
2/ 3/22	25°	88° 6′	129°	.111	18.0
2/ 4/22	74°	88° 47′	132.5°	.079	27.9
2/ 5/22	100°	88° 44′	133°	.084	26.8
2/ 6/22	25°	88° 7′	128.5°	.110	17.7

TABLE IV.

Potassium.

Date of Observation.	Temperature.	2ψ.	Δ.	n.	k.
1/7/22	54°	88° 39′	119° 30′	.062	19.3
1/9/22	73°	88° 40.8′	115° 8′	.057	23.6

TABLE V.

25.8 Per Cent. Sodium and 74.2 Per Cent. Potassium.

Date of Observation.	Temperature.	2ψ.	Δ.	n.	k.
9/11/21	Room	87° 25.2′	122.7°	.128	13.0
9/17/21	"	87° 19.4′	122.5°	.132	12.5
1/29/22	" (25° C.)	87° 27.4′	119.8°	.119	12.9
1/30/22	47°	87° 27.4′	119.8°	.119	12.9
2/ 1/22	65°	87° 28′	119.4°	.117	12.9
2/ 2/22	Room (25°)	87° 27.5′	119.9°	.118	12.9

Results given in Tables III., V., and Fig. 8, would indicate that the optical constants of the liquid alloys remain constant for the given ranges of temperature. In the case of the solid alloy (Table III. and Fig. 8) there is a very marked change in n and k resulting from the change in temperature and the process of fusion. However, from a consideration of the potassium mirror where heating was necessary to obtain a smooth surface and where the change in the optical properties for a change in state were within the limits of experimental error, it would be impossible to tell whether the changes found for n and k for the above solid alloy were actually due to a change in the optical properties, or were due to a surface effect. There may have been slight irregularities in the surface produced by the contraction of the metal from the glass which could not be detected by the eye, but which would cause an error in the observed values of 2ψ and Δ. It is possible that such a surface effect may be the cause for the difference in the results obtained for two potassium mirrors by R. W. and R. C. Duncan.[1] The difference between the results of Meese[2] and those of R. W. and R. C. Duncan for sodium and potassium may also be due to such an effect.

It is proposed to continue this work by making a more detailed study of the effect of the change of temperature upon the optical properties of sodium and potassium and perhaps some of the alloys.

In conclusion the writer wishes to acknowledge his indebtedness to Professor H. C. Richards for having suggested this problem and for his many valuable suggestions throughout the investigation.

Randal Morgan Laboratory of Physics,
University of Pennsylvania,
Philadelphia, Pa.

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[1] R. W. and R. C. Duncan, loc. cit.

[2] Meese, loc. cit.

RELATIVE INTENSITIES OF STARK EFFECT COMPONENTS IN THE HELIUM SPECTRUM.

BY JOHN STUART FOSTER.

SYNOPSIS.

Modified Lo Surdo tube for observing the Stark effect.—By placing the tube with its axis perpendicular to the slit and using the cross-section of the cathode afflux where the field is a maximum, separate and parallel components were obtained. Pitting of the aluminum cathode, however, causes a gradual shifting of the field and consequent blurring of the components with exposures of several hours, and this limits the usefulness of the method at present.

Relative intensities of the Stark effect components of the helium lines λλ 4922, 4472, and 4388 Å in a field of 15,000 volts/cm.—Spectrograms were taken of the p and s components in turn through a neutral wedge, using a five-prism spectrograph (Figs. 3–5); then energy distribution curves were calculated from the contour of the images and the corresponding wedge densities (Fig. 6), and the relative intensities were obtained by integration. The results for the main p components follow in order ot increasing wave-length: for the line 4388, 8.2 (isolated), 4.1, 19.2, 28.0; for 4472, 168, 694; for 4922, 9.7, 31.6. Corresponding results for the s components are: for 4388, 1.0 (isolated), 3.0, 11.3, 9.5; for 4472, 76, 464; for 4922, 6.2, 21.4.

INTRODUCTION.

IT is the purpose of the present paper to describe a new method for the observation of the Stark effect, and its application to the determination of relative intensities of components of lines in the helium spectrum.

As is well known, there are two distinctly different types of discharge tubes which have been commonly employed in the study of the Stark effect. (*a*) Stark[1] and his fellow workers have used, initially, the canal-ray tube in which the canal rays upon passing through the perforated cathode enter a uniform field between the cathode and an auxiliary electrode. The light is not intense; certain lines do not appear (notably Fowler's enhanced helium series beginning with λ 4686, of theoretical interest); but the method has a very great advantage in that the field strength is known directly. It has been customary to use two current sources, one of which must supply direct current. The components appear separate and parallel on the plate. (*b*) Lo Surdo[2] first used the method employing the electric field in the cathode fall. A variety of tubes of the Lo Surdo type have been used and the field distribution changes with the tube design. The light from the center of the stream immediately in front of the cathode in a tube of small diameter is more intense than that from a canal-ray tube, and Fowler's series is present. Field strengths are found indirectly through the separation of well-known components, which have been carefully studied in the canal-ray tube. In all previous investigations the axis of the tube has been parallel to the slit of the spectrograph so that, due to the variable field, the components appeared on the plate as curved lines.

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[1] J. Stark, Elektrische Spektralanalyse chemischer Atome, Leipzig, S. Hirzel, 1914.

[2] A. Lo Surdo, Rendiconti d. Lincei, 22, 664, 1913.

The writer has undertaken the problem of finding the relative intensities of Stark effect components by means of a neutral wedge.[1] Obviously the canal-ray tube might have been used, though it supplies a relatively weak source. It should prove satisfactory for intensity measurements in the Balmer series, and elsewhere of less immediate theoretical interest. At the time this work was started, however, this tube had not been used with a single source of current[2] and as two satisfactory sources were not available it was decided to use a Lo Surdo tube with helium as the gas. The usual source of light in the latter tube consists of a thin section cutting through the center of the stream; and includes not only the bright central portion, but an equally thick part of the less intense outer portion. The resulting spectrograms show well-defined components which fact indicates that in a cross-section of the stream at any point the field is effectively constant or nearly so.

If the field throughout the cross-section be constant or nearly constant, either actually or effectively, then the main components of a line should be separate and parallel if the tube be used with its axis perpendicular to the slit. It thus appears to be possible to obtain with a Lo Surdo tube components which have the same appearance on the plate as those from a canal-ray tube. The neutral wedge method for intensity measurement is equally applicable, and there are the advantages of more light and more lines.

The form of tube first described by Nyquist[3] was selected as a good one with which to start the investigation. In this tube the field distribution is such that there is a maximum value so that for a short distance along the axis of the tube the field is nearly constant. If the image of this section of the source be allowed to drift across the slit during an exposure, then the blurring of the components, due to cathode pitting, will be a minimum.

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[1] J. W. Nicholson and T. R. Merton, Phil. Trans., Ser. A, 216, 459, 1916.

[2] F. Tuczek and W. Heuck, Ann. d. Phys., 63, 766, 1920.

[3] H. Nyquist, Phys. Rev., 10, 226, 1917.

The reader is referred to the original paper by Nicholson and Merton[1] for the theory of the wedge. The relative energy content of two components is given by

$$\frac{\int I_{\lambda_1} d\lambda_1}{\int I_{\lambda_2} d\lambda_2}$$

where the subscripts refer to the components. I_λ is the intensity of monochromatic light of wave-length λ which has just penetrated the first surface of the wedge. The above may be written

$$\frac{\int \log_{10}{}^{-1} \frac{h_{\lambda_2} D_\lambda}{M} d\lambda_1}{\int \log_{10}{}^{-1} \frac{h_{\lambda_2} D_\lambda}{M} d\lambda_2},$$

where $\log_{10}{}^{-1}(h_\lambda D_\lambda / M)$ is defined as the photographic intensity of light of wave-length λ. The height h_λ of a component varies over its width in accordance with the distribution of energy and is measured on an enlargement of magnification M. D_λ is the change in the density of the wedge per millimeter of its length, for light of wave-length λ. It may be assumed constant over the region including the components of any one line herein investigated. The dispersion of the spectrograph, too, is similarly constant. Thus it is easy to construct energy distribution curves for the components of a line, from the contour of the enlarged images and the corresponding wedge densities. From such curves the relative intensities of the components may be found by means of a planimeter.

EXPERIMENTAL.

The helium, prepared from thorianite and initially at atmospheric pressure, is kept in a bulb which is attached to the main vacuum apparatus by a tube in which there is a stopcock and a constriction. Thus the gas can be admitted to the vacuum in any desired quantity. The arrangement is such that it can be forced around a circuit, and a charcoal bulb immersed in liquid air is used to keep it pure. A transfer pump helps to circulate the gas and to regulate the pressure in the discharge tube. A ballast capacity of three liters tends to keep the pressure constant.

The discharge tube is of pyrex glass, and is shown in Fig. 1. It consists of a main portion M, of 1.3 cm. internal diameter, which supports the aluminium anode A; and an auxiliary tube B, which insulates the greater part of the cathode rod C. The two glass parts B and M are sealed together with hard wax. The cathode is an aluminium rod 3.5 mm. in diameter; and is supplied with two collars, which fit *B* as closely as possible. It is held in position by a coiled steel spring, which presses one of the collars against the surrounding tube at a point where the latter is purposely dented. The space between the rod and the glass wall is 0.5 mm. wide. Between the glass tubes *M* and *B*, and fitted closely to each, is a hollow cylinder of aluminium *D*. A small portion of this is in the form of a thin-walled tube and lies inside *B*. This part of *D* has an internal diameter of 3 mm., ends 7 mm. from the cathode surface, and does not touch the glass walls. The side tube S_3 is placed opposite the cathode surface and is 4 cm. long. The window *W* is sealed to this tube with wax. Narrow slits are made through *B* and *D*. The side tubes S_1 and S_2 form a part of the circuit around which the helium may be forced. The useful life of a tube of this type is about sixty hours.

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[1] Loc. cit.

The discharge is very stable. It is necessary, however, to have constant communication with the charcoal bulb. In one half hour from the time the tube is started, it is possible to increase the pressure to 3 mm. of mercury with safety. During this time a pit in the cathode is started. This pit apparently grows as long as the tube lasts. In a tube 60 hours old it is 2.8 mm. deep and the diameter is exactly equal to that of the aluminium tube close to the cathode. The greater part of the pit is uniform in diameter. The bottom is conical. The tube may be run without any cooling device, provided the current does not exceed 3 mil. amps. During an exposure of 7 hours no change could be detected in the voltage or current. In the longest exposure (18 hours) there were a few slight fluctuations. Corrections were immediately made by adjustment of the ice-cooled water resistance or the pressure of the helium. The variation was never more than one per cent. of the total. It follows that the variation in the field to which the source is subjected, which comes as a result of irregularity in the discharge, is no greater than that due to ripples in the rectified current, and is less than that caused by the drift and redistribution of electric field which accompanies the pitting of the cathode.

The source of direct current is essentially that described by Nyquist.[1]

Immediately in front of the window of the discharge tube is a Bausch and Lomb Tessar lens of 5 cm. focal length and 1.2 cm. aperture. A double-image prism, placed close to the lens, separates the images, which are double the size of the source. At the focal plane a diaphragm stops one of the images. A sphero-cylindrical lens is so placed that the images formed by the Tessar lens are in the principal plane of the spherical portion the focal length of which is 7.5 cm. The light is focused on the slit by the cylindrical portion of 15 cm. focal length. On the cylindrical surface is a diaphragm with a square opening 5.6 mm. on each side. This is just filled with light by the Tessar lens.

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[1] Loc. cit.

The wedge is of dense neutral glass supplied and ground by Brashear. At the thick end it is very dark, though not visually opaque to daylight. The neutral glass is cemented to a wedge of colorless glass such that the two pieces form a plane parallel plate. The colorless glass extends beyond and protects the knife edge of the neutral glass. The wedge is mounted on a slide immediately in front of the slit. The opening in the slide is 5 mm. long. One end of this opening matches the thin end of the wedge.

The collimator and camera lenses are doublets of 45″ focal length and 3″ aperture. They were designed by Professor Hastings and ground by Brashear from glass especially transparent to light in the visible region.

The dispersive apparatus consists of five glass prisms with circular faces 6 cm. in diameter. They are on a base of cast iron which is accurately flat. The dispersion is 4.0 Å./mm. at λ 4472.

RESULTS.

The lines λ 4922, 4472, and 4388 were examined. Of these, 4922 and 4388 are the second and third terms respectively of the second subordinate series of parhelium.[1] The first term is 6678. The line 4472 is the second term of the diffuse series in the system of pairs. The first three members of this series are λ 5876, 4472, and 4026.

Seed 30 plates were used. The even illumination of the slit is shown in Fig. 2. On the negative from which this figure is taken one can clearly see the "isolated component" of 4922, observed by many investigators, and classified by Liebert[2] as the first term of the "new" third subordinate series. This line is weak, and does not show on the plates taken with the wedge in position. The "isolated component" of 4388, the second term of the above-mentioned new series, is caught at a point where, as the wedge spectrogram shows more clearly, it is beginning to break into the two components observed by Nyquist and by Takamine and Kokubu.[3]

After making sure of even illumination of the slit, the wedge was placed in position and an exposure of seven hours was made. The resulting plate, No. 12, is the one from which all measurements of the

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[1] F. A. Saunders, Astrophys. Journ., 50, 151, 1919.

[2] G. Liebert, Ann. d. Phys., 56, 610, 1918.

[3] T. Takamine and N. Kokubu, Mem. Coll. of Sci., Kyoto, 3, 275, 1919.

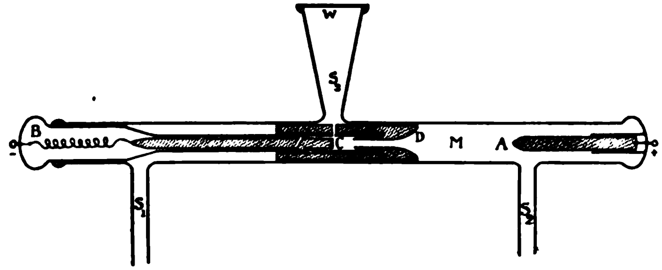
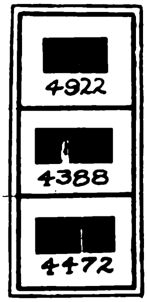
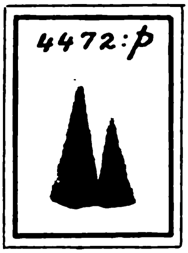
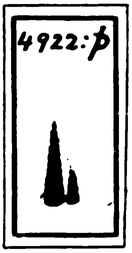


Fig. 1.







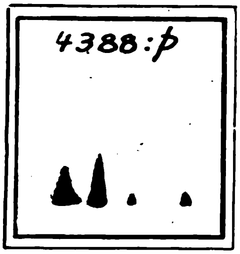


Fig. 2.　　Fig. 3.　　Fig. 4.　　Fig. 5.

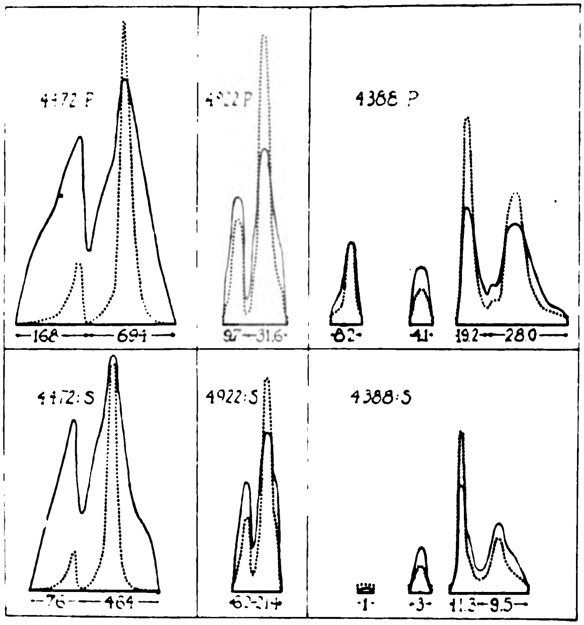


Fig. 6.

J. S. FOSTER.

p components are taken. It is thought to be reliable, because no change was detected in the voltage or current during the exposure. The voltage on the tube was 6000 v.; the current 3 mil. amp.; and the pressure of the helium was 2.8 mm. Figs. 3 and 4 are enlargements of the images of 4472 and 4922 respectively, and are taken from plate No. 12. Fig. 5 is an enlargement of 4388 and is taken from a plate exposed for a longer period. The s components are taken from a plate exposed for eight hours under conditions similar to those under which No. 12 was obtained. The field strength is found from the separation of the main components of 4472.

The continuous lines of Fig. 6 represent the contours of all lines examined. As the background of the plate was quite clear, the enlargements were sketched directly, through the aid of an instrument commonly used by biologists for the sketching of slides. The distortion was small and the error arising therefrom is considered less than that due to imperfectly judging a contour of constant density. The latter operation involves an error of about one per cent.

It is, of course, evident that the unit used herein for intensity measurements is that intensity which under the photographic conditions produces an effect on the plate, which is just visible. Therein lies a great advantage of the wedge method, for the investigator need know nothing about the behavior of the plate toward the various frequencies and intensities of light; and encounters no difficulties due to irradiation. In order to draw the energy distribution curves for a group of components, one needs to know the following quantities only: (i) D_λ, the change in wedge density per millimeter length of wedge, for the average frequency of light involved; (ii) a series of values of h_λ, the height of the image, at various points over the widths of the components; and (iii) M, the magnification of the enlargement on which the heights are conveniently measured. The ratio h_λ/M gives, so far as we can detect, the length of wedge penetrated. The physical meaning of D_λ is seen from the following consideration. Let two constant sources of monochromatic light of wave-length λ_0 and of intensities $A > B$ be such that, for otherwise identical photographic conditions, the length of wedge penetrated by the light of intensity A exceeds by *one millimeter* the length penetrated by the light of intensity B; then $\log_{10} A/B = D_{\lambda_0}$.

Because the energy distribution quite clearly varies with the components, at least under ordinary conditions of electric field, dispersion, and resolution, the heights[1] of the components are inadequate for the accurate determination of relative intensities. If, however, the heights be measured at a large number of points over the width of each component or group of unresolved components, and be used, together with the wedge density, to plot the distribution curves; then a much closer approximation is obtained. This has been done. The dotted lines in Fig. 6 represent the energy distribution. Under each main component will be found the relative energy content which has been assigned to it. There remains, nevertheless, an error which is at present hard to evaluate. This is due mainly to a variation of the field, which variation affects the position of each real component to a degree dependent upon the distance from the original line. Thus the outside components are the most blurred.

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[1] J. W. Nicholson and T. R. Merton, loc. cit.; also Phil. Trans., A., 217, 231, 1917.

The usefulness of the present method is limited, therefore, by the cathode pitting which produces the effect just mentioned. Unless conditions be changed, longer exposures will be required to obtain measurements of Fowler's series, and longer exposures will produce a blurring which may seriously affect the accuracy. Nevertheless, it is well known that the Lo Surdo method has led to the discovery of new lines, in fact new series of lines, with exposures which under ordinary conditions of spectrographic apparatus were for periods of a few hours. Also the writer has observed that in an aged horizontal tube the analysis obtained with short exposures is apparently quite equal to that produced by means of a canal-ray tube. It has seemed worth while, therefore, to investigate further the possibilities of the method herein outlined. A design of tube which will reduce or eliminate the cathode pitting seems the most probable way out of the difficulty.

The extension of the investigation has been made possible by the National Research Council.

The writer wishes to express here his deep indebtedness to the late Professor Henry Andrews Bumstead, who proposed the problem, devised the method of attack, and gave direction and encouragement during the first part of the work. He desires also to extend his best thanks to Professor Leigh Page for his interest and direction. His thanks are further due to Professor H. S. Uhler, whose exact information and advice regarding spectroscopic apparatus have removed many difficulties.

SLOANE LABORATORY,
YALE UNIVERSITY,
April, 1922.

QUENCHING: A MATHEMATICAL STUDY OF VARIOUS HYPOTHESES ON RAPID COOLING.

By K. Heindlhofer.

Synopsis.

Mathematical Study of the Temperature Changes in a Hot Body after Quenching, Assuming Various Conditions of Heat Flow from the Surface.—(1) Assuming no thermal resistance at the surface, theoretical cooling curves for a steel ball and a steel plate are computed (Fig. 1). (2) Assuming constant thermal resistance, the general equation is derived for the case of a cylinder of finite length (Eq. 17). (3) Assuming a vapor layer which conducts the heat to a liquid layer at rest, the general solutions for the temperatures at the surface of a large body (Eq. 41) and of a plate (Fig. 5) are obtained. (4) Assuming that the heat after passing through the vapor layer is carried away by convection at a uniform rate, the equation and curves are obtained for the case of a plate (Eq. 58; Fig. 6).

Heat Flow from a Metal Cylinder Quenched in Water.—By comparing various experimental cooling curves with the theoretical curves obtained above, it is evident that after the first stage of quenching none of the assumed conditions correspond to the facts. It is found that the rate of transfer of heat through the surface is not constant but is an exponential function of the temperature of the surface. Smaller cylinders seem to have less specific heat flow. The discrepancy with theory is doubtless due to the neglect of the bubbling which begins almost immediately.

Reheating of the surface of a body immediately after quenching, due to sudden formation of a steam jacket, does not occur. Reheating as evidenced by structural investigation may occur in a later phase of quenching.

I. Hypothesis No. 1.

Sudden cooling of the surface to final temperature.

This hypothesis has been dealt with by Fourier.[1] It presupposes a quenching medium, the cooling effect of which is infinitely rapid. The cooling of the solid depends then entirely on its thermal and geometrical properties.

The conclusions which are derived from this hypothesis are of value in certain cases. A body with high specific heat capacity and low conductivity will evidently be cooled very rapidly at the surface. Another case where this hypothesis is effective is the central portion of a large body, which is very little depending on the quenching medium. This may be clear when it is considered that after the surface has cooled, the flow of heat to the surface will rapidly diminish on account of the thick layer interposed between the hot interior and the cold surface. This will be proven in the next section.

On the other hand, the temperature in small bodies of high diffusivity is inaccurately represented by this hypothesis. The inaccuracy is greatest at the surface itself.

The hypothesis under consideration represents the extreme, the ideal which may be approached, more or less. If applied to the sphere, the temperature distribution is as follows:

$$\frac{u - u_0}{u_i - u_0} = \frac{2R}{\pi \rho} \sum_{m=1}^{\infty} (-1)^{m+1} \frac{1}{m} e^{-m^2 a^2 (\pi/R)^2 t} \cdot \sin\left(m\pi \frac{\rho}{R}\right), \tag{1}$$

u_i initial temperature (assumed to be uniform at time $t = 0$),
u temperature at the radius ρ,
u_0 final temperature or temperature of the quenching medium,
ρ variable radius,
R radius of the sphere,
t time,
a^2 diffusivity. For steel we assume $a^2 = 0.111$ cm.^{2}/sec.

The corresponding equation for the center of an infinite slab is

$$\frac{u - u_0}{u_i - u_0} = \frac{4}{\pi} \sum_{m=1}^{\infty} \frac{(-1)^{m+1}}{2m - 1} e^{-(2m-1)^2 a^2 (\pi/2l)^2 t}, \tag{2}$$

where l is half the thickness of the slab.

Figs. 1*a* and 1*b* and the three-dimensional model Fig. 1*c* shows temperature distribution in a steel ball of 1 cm. radius, assuming fastest possible quenching, *i.e.*, given by equation (1). The values shown in Fig. 1 may be used to determine the temperature in any sphere with any thermal constants as the exponent in equation (1) remains unchanged

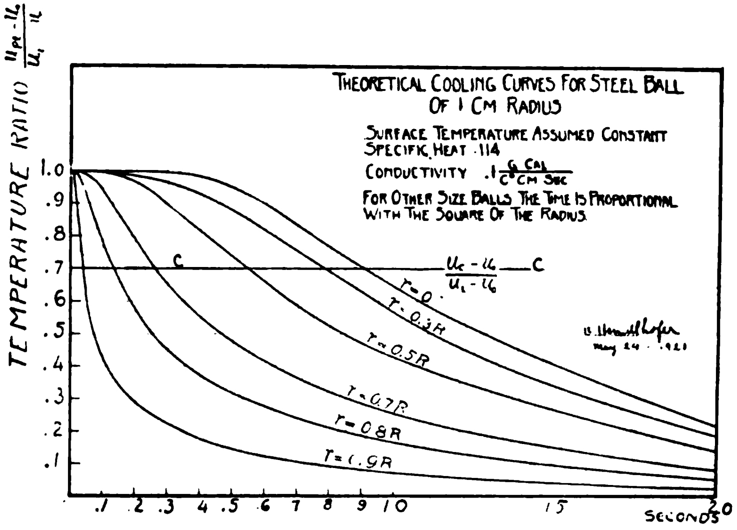

Fig. 1*a*.

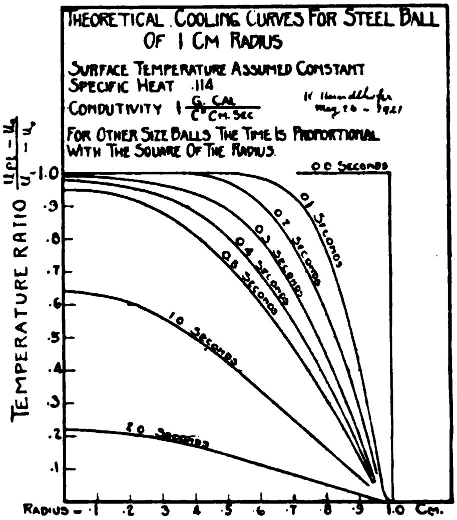

Fig. 1*b*.

if t is increased in the same proportion as R^2 and inversely as a^2. From this it is obvious that in order to derive new diagrams from the old one for other values of R and a^2, it is only necessary to change the abscissa scale to suit.

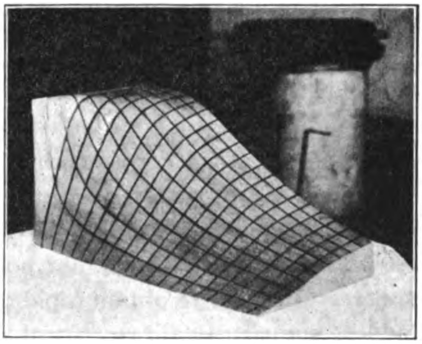

Fig. 1*c*.

Fig. 1*d* shows the curves of Fig. 1*a* on semi-logarithmic paper. Equation (2) is plotted in Fig. 2. The steady flow condition in this case appears as a straight line and the slope of the lines representing temperature-time in various depths, is the same. Thus the logarithmic plotting has the advantage of simplicity, furthermore, it is valuable in deciding whether an experimental cooling curve follows the exponential law.

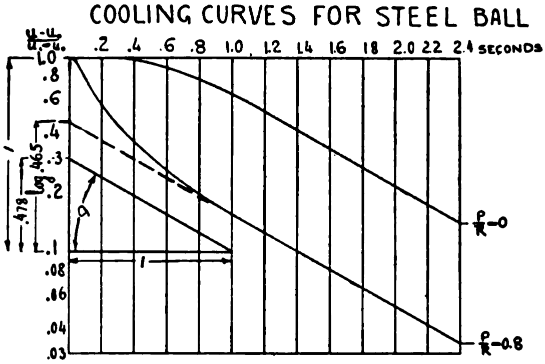

Fig. 1*d*.

Fig. 1*a* may be useful to demonstrate the effect of over-heating of steel on its ultimate hardness. It has been shown[2] that the quenching speed of steel through the transformation range, is the determining factor for the resulting hardness. There is a critical cooling speed, below which soft structure with more or less troostite is formed and above which hard structure with pure martensite or martensite plus austenite, is produced. Thus the slope of the curves at the transformation range is of interest.

The ordinates in Fig. 1*a* are expressed in relative units. As the total temperature drop is chosen for unit, all other temperatures will be expressed in fractions of this unit. In order to see the influence on the speed of cooling by raising the quenching temperature to higher values, it is not necessary to replot the curve, but it is sufficient to drop the line *CC*. The slope of the temperature-time curve at the intersection with *CC*, represents the cooling speed at the corresponding point. An inspection of the curve shows that an initial temperature only slightly above the transformation point cannot result in rapid cooling through the transformation range. This is especially true for points in the vicinity of the center of the sphere. In order to obtain rapid cooling, the quenching temperature should be sufficiently above critical. This is in accordance with experience.

II. HYPOTHESIS NO. 2.

Heat emitted by a unit area in a unit time is proportional to the difference between the surface temperature and the temperature of the quenching liquid (Newton's cooling law). This is equivalent to assuming a constant surface resistance.

Newton's cooling law, *i.e.*, law of surface emission of heat which does not assume instantaneous cooling of surface, may be written

$$- K\left(\frac{\partial u}{\partial x}\right)_s = H(u_s - u_0), \tag{3}$$

where K = conductivity of the metal,
H = constant surface cooling,
u_s = variable surface temperature,
u_0 = temperature of the quenching liquid at a great distance from the quenched body. u_0 is assumed to be constant.
S indicates surface.

Equation (3) may be interpreted in two ways, viz.:

(*a*) The amount of heat emitted by a unit area in a unit time is proportional to the difference between the surface temperature and the temperature of the surrounding medium.

(*b*) Imagine an insulating layer on the surface. Let the temperature on the two sides of this layer be u_s and u_0. Let the thickness of the layer be "d" and assume d small, *i.e.*, the heat capacity negligible. Its conductivity should be low enough to have appreciable effects in spite of the small thickness. According to the fundamental conception of heat conduction

$$- K' \frac{u_0 - u_s}{d} = - K\left(\frac{\partial u}{\partial x}\right)_s.$$

If K'/d be set equal to H, equation (3) is obtained, which proves that *Newton's cooling law may also be interpreted as a constant surface resistance obstructing emission of heat.*

The problem of heat flow under the assumption of equation (3) was solved by Fourier and Poisson for the sphere, the slab, the prism, the cube, and the infinite cylinder.

In order to compare the two types of coolings defined by Hypotheses 1 and 2 respectively, consider the cooling equation for an infinite plate as given by Poisson:

$$\frac{u-u_0}{u_i-u_0} = \sum_{m=1}^{\infty} e^{a^2\lambda^2_m t}\cdot\left[\frac{\lambda_m \cos(x+l)\lambda_m + \frac{H}{K}\sin(x+l)\lambda_m}{\frac{H}{K} + l\left(\frac{H^2}{K^2}+\lambda_m^2\right)}\right]\left[\sin(\lambda_m 2l) + \frac{H}{K\lambda_m}(1 - \cos\lambda_m 2l)\right], \tag{4}$$

$$tg(\lambda_m l) = \frac{H}{K}\frac{l}{\lambda_m l}, \tag{5}$$

$$tg(\lambda_m l) = -\frac{\lambda_m l}{l}\cdot\frac{K}{H}. \tag{6}$$

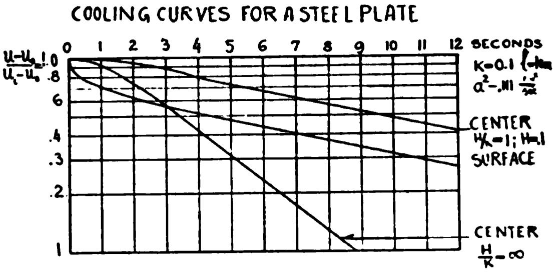

Fig. 2.

Equation (4) is plotted on Fig. 2 for a steel plate, 2 cm. thick with a diffusivity $a^2 = 0.111$ and $H = 0.1$.

The extreme cases of great surface emissivity on the one hand and great thickness of the plate on the other, are of interest. For these cases either H/K or l approach infinity and equation (5) becomes

$$\lambda_m l = (2m - 1)\frac{\pi}{2}.$$

Substituting this into equation (4) the latter becomes for $x = 0$ the same as equation (2), which proves the statement made in the second paragraph of Section 1, that in case of large bodies the cooling at the center does not depend much on the value of the surface emissivity H/K as long as H/K is not too small. *In practice this would mean that quenching speed cannot be improved at the center of a bulky piece of metal by substituting water in place of oil.*

Due to the fact that a great number of quenching experiments were conducted on cylinders the height of which is comparable with their diameter, the solution for the cylinder of finite length is important. In order to solve it, let us make Fourier's equation in cylinder coördinates, our starting point.

(7) $$\frac{\partial u}{\partial t} = a^2\left(\frac{\partial^2 u}{\partial \rho^2} - \frac{1}{\rho}\frac{\partial u}{\partial \rho} - \frac{\partial^2 u}{\partial z^2}\right).$$

This equation is satisfied by the particular solution:

(8) $$u = xe^{-mt}\cos pz,$$

where x is a new variable depending on ρ only. Substitute (8) in (7)

(9) $$\frac{\partial^2 x}{\partial \rho^2} + \frac{1}{\rho}\frac{\partial x}{\partial \rho} + \left(\frac{m}{a^2} - p^2\right)x = 0.$$

This is the differential equation of the Bessel functions. The solution is

(10) $$x = J_0\left(\rho\sqrt{\frac{m}{a^2} - p^2}\right).$$

Therefore the particular solution (8) becomes

$$u = J_0\left(\rho\sqrt{\frac{m}{a^2} - p^2}\right)e^{-mt}\cos pz. \tag{11}$$

At the curved surface $\rho = R$ Newton's cooling law (eq. 3) should be satisfied by (11).

$$H(u)_{\rho=R} + K\left(\frac{\partial u}{\partial \rho}\right)_{\rho=R} = 0. \tag{12}$$

Set

$$\frac{H}{K} = h \tag{13}$$

and

$$\frac{m}{a^2} - p^2 = \lambda_m^2. \tag{14}$$

From (11), (12), (13) and (14) we obtain

$$\frac{Rh}{R\lambda_m} = \frac{J_1(R\lambda_m)}{J_0(R\lambda_m)}. \tag{15}$$

For the flat sides the procedure is similar and

$$\frac{bh}{bp} = tg(bp) \tag{16}$$

is obtained where $2b$ is the length of the cylinder. Both equations (15) and (16) have an infinite number of roots; each one determines a particular solution, which fulfills surface conditions.

From equations (11) and (14) the general solution will be:

$$\begin{aligned} u = {} & \left[a_1J_0(\rho\lambda_1)e^{-a^2\lambda_1^2t} + a_2J_0(\rho\lambda_2)e^{-a^2\lambda_2t} + \cdots\right]\left[b_1\cos(p_1z)e^{-a^2p_1^2t}\right. \\ & \left. + b_2\cos(p_2z)e^{-a^2p_2^2t} + \cdots\right] \end{aligned} \tag{17}$$

The constants a_m and b_m may be determined according to Fourier. Their values are

$$a_m = u_i\frac{\dfrac{1}{\lambda_m}J_1(R\lambda_m)}{\dfrac{R}{2}\left[1+\left(\dfrac{hR}{2\sqrt{\lambda_m}}\right)^2\right]J_0^2(R\lambda_m)}; \quad b_m = u_i\frac{2\sin(p_mR)}{P_m\left[R+\frac{1}{2}\dfrac{\sin(2p_mR)}{p_m}\right]} \tag{18}$$

where u_i is the initial temperature of the cylinder.

III. Hypothesis No. 3a.

Steam is formed at the boundary of the solid (Leidenfrost effect). The *water-steam surface remains parallel with the surface of the solid. Heat moves in the liquid by conduction alone.*

In quantity production of hard steel articles such as balls and races for bearings, it was in some instances found that the outer surface of the quenched steel had soft spots which covered material of normal hardness. Structural investigation with the microscope indicated that a reheating of the surface, while quenching to a depth of a few tenths of a millimeter, had taken place.

In the following it is attempted to investigate mathematically the conditions under which a reheating of the surface occurs. It was suggested that at the instant of quenching the surface layer cools considerably. Immediately after this steam is formed which arrests any further cooling. The surface is then reheated by the hot central portion of the metal. In turn it will be shown that this view is not correct. At best, reheating may eventually occur in a later phase of the quenching, when local accumulation of steam has taken place.

Infinitely extended body with plain boundary.

In order to be able to treat the problem mathematically, it is necessary to choose the simplest conditions, *i.e.*, an infinite plainly bounded solid (Fig. 3). Furthermore, it will be assumed that the thickness of the steam layer formed is uniform; in other words, the boundary of the vapor and liquid remains parallel with the surface of the solid. This must be true as long as the steam layer is very thin. Assume that a bulging out would start at "*a*." Immediately the poorly conducting layer would be increased in thickness, which in turn would reduce heat conduction at "*a*," counteracting further evaporation. In case of an approach "*b*" the opposite would happen. The evaporation would then tend to stabilize the surface of the liquid and would keep it of uniform thickness. With greater thickness the unevenness of the surface becomes relatively small, thus the stabilizing effect decreases, and the surface becomes unstable, and will break up into bubbles. The subsequent investigation should be regarded as an approximation and should be restricted to a short time interval, immediately after immersion. The main object is to decide whether or not a reheating may take place during this interval.

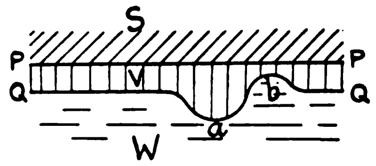

Fig. 3.

The phenomenon of soft surface occurs in water quenching of steel. We shall restrict our constants to steel, steam and water.

Notation.

Value of Constants Assumed in the Calculation.

$$K = \text{coefficient of heat conductivity} \begin{cases} \text{For steel we assume} \,..\, K_1 = 0.1 \dfrac{\text{g cal.}}{\text{cm. sec. C.}^\circ}; \\ \text{For superheated steam } K_2 \sim 10^{-4} \dfrac{\text{g cal.}}{\text{cm. sec. C.}^\circ} \text{average v.}; \\ \text{For water} \,\ldots\ldots\ldots\, K_3 \sim 1.4 \times 10^{-3}. \end{cases}$$

$$\rho = \text{density} \ldots\ldots \begin{cases} \text{Steel} \ldots\ldots\ldots\ldots \rho_1 = 7.8 \text{ g/cm.}^3; \\ \text{Superheated steam} \ldots \rho_2 = 3.10^{-4} \text{ g/cm.}^3 \text{ average}; \\ \text{Water} \ldots\ldots\ldots\ldots \rho_3 = 1.0. \end{cases}$$

$$c = \text{specific heat} \begin{cases} \text{Steel} \ldots\ldots\ldots\ldots C_1 = 0.114; \\ \text{Superheated steam} \ldots C_2 = 0.5\text{—average value}; \\ \text{Water} \ldots\ldots\ldots\ldots C_3 = 1.0. \end{cases}$$

m = volume ratio steam/water = $\rho_3/\rho_2 = 3.33 \times 10^3$.
$a^2 = K/\rho C$ = diffusivity.
x = depth coördinate $x < 0$ within the steel.
$x = \xi$ boundary QQ (water, steam) at time t. (See Fig. 4.)
ξ' = thickness of layer of water which evaporated at time t.
λ = heat of evaporation (latent h). 540 cm. sec.
$\Theta(x) = 2/\sqrt{\pi}\int_0^x e^{-\beta^2} d\beta$ abbreviation for the probability integral.
u = temperature.
t = time.

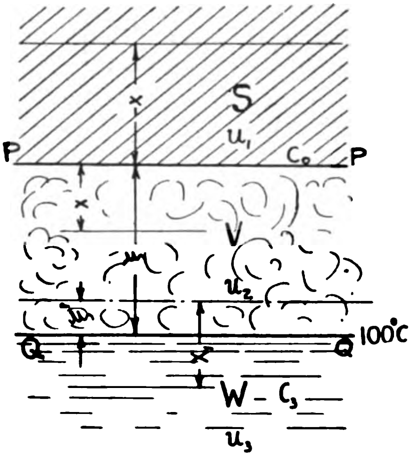

Fig. 4.

A, *B*, *C*, constants to be determined from the limiting conditions α, β are constants.

The differential equations governing the flow of heat are

$$(19)\qquad \frac{\partial u_1}{\partial t} = a_1^2 \frac{\partial^2 u_1}{\partial x^2} \text{ in the steel,}$$

$$(20)\qquad \frac{\partial u_2}{\partial t} = a_2^2 \frac{\partial^2 u_2}{\partial x^2} \text{ in the steam,}$$

$$(21)\qquad \frac{\partial u_3}{\partial t} = a_3^2 \frac{\partial^2 u_3}{\partial x_1^2} \text{ in the water.}$$

At the plane QQ the heat of evaporation per second must equal the difference between gain and loss per second at the plane QQ, which gives the following equation:

$$(22)\qquad K_2\left(-\frac{\partial u_2}{\partial x}\right)_{\xi} = K_3\left(-\frac{\partial u_3}{\partial x_1}\right)_{\xi'} + \lambda \rho_3 \frac{d\xi'}{dt}\,.$$

It may be verified by substitution, that the solutions of these differential equations are

$$(23)\qquad u_1 = A_1 + B_1\Theta\left(-\frac{x}{2a_1\sqrt{t}}\right);$$

$$(24)\qquad u_2 = A_2 + B_2\Theta\left(\frac{x}{2a_2\sqrt{t}}\right),$$

$$(25)\qquad u_3 = A_3 + B_3\Theta\left(\frac{x_1}{2a_3\sqrt{t}}\right)$$

$$(26)\qquad \xi = \alpha\sqrt{t}$$

$$(27)\qquad \xi' = \beta\sqrt{t}$$

$$(28)\qquad \alpha = (m + 1)\beta.$$

The boundary conditions to be fulfilled are

$$x_1 = \xi', \qquad x = \xi, \qquad u_2 = u_3 = 100^\circ \text{ C}.$$

from (24), (25), (26), (27)

$$(29)\qquad A_2 + B_2\Theta\left(\frac{\alpha}{2a_2}\right) = 100,$$

$$(30)\qquad A_3 + B_3\Theta\left(\frac{\beta}{2a_3}\right) = 100.$$

for $x = 0$, $u_1 = A_1$; $u_2 = A_2$ denote

(31) $$A_1 = A_2 \equiv C_0,$$

let the temperature of the water far away from the plate be $x_1 = \infty$, $u_3 \equiv C_3$, then

(32) $$C_3 = A_3 + B_3$$

from (29) and (31),

(33) $$B_2 = \frac{100 - C_0}{\Theta\left(\frac{\alpha}{2a_2}\right)}$$

from (30) and (32)

(34) $$B_3 = \frac{C_3 - 100}{1 - \Theta\left(\frac{\beta}{2a_3}\right)}.$$

We assume the initial temperature of the steel C_1, uniform at $t = 0$ and

(35) $$u_1 \equiv C_1 \quad \text{for} \quad x = -\infty$$

from

(36) $$C_1 = A_1 + B_1$$

from

(37) $$u_1 = C_0 + (C_1 - C_0)\Theta\left(\frac{-x}{2a_1\sqrt{t}}\right).$$

In order to determine C_0 we have to remember that the gain and loss of heat at the boundary of the metal are equal, thus

(38) $$K_1\left(-\frac{\partial u_1}{\partial x}\right)_{x=0} = K_2\left(-\frac{\partial u_2}{\partial x}\right)_{x=0}$$

if the values u_1 and u_2 from (23) and (24) be substituted

(39) $$-\frac{K_1B_1}{a_1} = \frac{K_2B_2}{a_2},$$

substituting the values for B_1 and B_2

(40) $$C_0 = \frac{100 + C_1\frac{K_1a_2}{K_2a_1}\Theta\left(\frac{\alpha}{2a_2}\right)}{1 + \frac{K_1a_2}{K_2a_1}\Theta\left(\frac{\alpha}{2a_2}\right)}$$

from (22) we obtain

$$C_0 = 100 + \left[\lambda \rho_3 \frac{\sqrt{\pi}}{2} \frac{a_2}{K_2} \Theta\left(\frac{\alpha}{2a_2}\right) \beta e^{(1/2a_2)^2\alpha^2} + \frac{a_2 K_3}{a_3 K_2} \frac{100 - C_3}{1 - \Theta\left(\dfrac{\beta}{2a_3}\right)} \Theta\left(\frac{\alpha}{2a_2}\right) e^{(1/2a_2)^2\alpha^2 - (1/2\beta_3)^2\beta^2} \right]. \tag{41}$$

(40) and (41) contain α and C_0 as the only unknown quantities.

Introducing the numerical values of the constants it is possible to determine by trial the values of α and C_0. For steel and water of the temperature of 0° C.

$$C_1 - C_0 = 12.6^\circ \text{ C.}$$

and

$$\alpha = 0.0336 \text{ cm. sec.}^{-1/2}. \qquad \text{(See Fig. 9.)}$$

This means that the temperature at the surface of an infinite body of steel drops 12.6° C. when quenched in ice cold water and remains at that temperature. The temperature gradually drops to this value within the body as per equation (37).

It would be interesting to compare the heat per second lost by conduction with that used for evaporating the water.

$$\frac{Q_C}{Q_\lambda} = \frac{\dfrac{K_3}{a_3}\dfrac{C_3 - 100}{1 - 0} m}{\lambda \rho_3 0.886 \alpha} = \frac{\dfrac{1.4 \times 10^{-3}}{0.0374} \times 100 \times 3.33 \times 10^3}{540 \times 1 \times 0.886 \times 0.0336} = 775.$$

From this we arrive to the conclusion that the latent heat is negligible compared with the conducted heat. This is explained by the great expansion of the water when converted to steam. *A very slight evaporation causes a comparatively great increase of thickness of the steam layer* thus decreasing the outflow of heat, while the heat conducted away is independent of the thickness of the steam layer. This holds good until the thickness of the steam layer becomes large enough to render it unstable and bubbles begin to form. Then the layer is broken down and new contact is formed, new evaporation sets in and the cooling will proceed at a higher rate than obtained by equation (37). Vigorous bubbling takes place also when quenching steel in hot water and by the evaporation at repeated contacts, it is possible to obtain hard quenching even in boiling water.

Plate of finite thickness, quenched on both sides.

In the preceding section it was shown that the surface temperature of a large piece of steel quenched in water will suddenly drop by an insignificant amount, and remain at that temperature, provided the assumptions on which the solution of the problem is based are fulfilled. When quenching large masses of steel it may actually be noticed that the surface remains incandescent for a considerable length of time after submersion.

Furthermore, it is borne out that under these assumptions a *temperature rise after the first drop would not occur.*

It would be of further interest to extend the investigation to a plate of finite thickness quenched at both sides. Evidently the solution would be identical with the one of the preceding section until the temperature drop reached the center of the plate; after this the surface temperature must gradually drop below C_0.

1. The amount of heat absorbed by the water at QQ (Fig. 4) may be easily determined as QQ must be at the constant temperature of 100° C. The classical solution (convection excluded) is

$$u_3 = 100\left(1 - \Theta\left[\frac{x_1}{2a_3\sqrt{t}}\right]\right). \tag{42}$$

The heat current thus is

$$K_3\left(\frac{\partial u_3}{\partial x_3}\right) = -100K_3\left[\frac{2}{2a_3\sqrt{\pi t}}e^{-(x_1/2a_3\sqrt{t})^2}\right]_{x_1=0} = -100K_3\frac{1}{a_3\sqrt{\pi t}}. \tag{43}$$

2. This same heat current must be emitted by PP (Fig. 4) as the capacity of the film, and the heat used in evaporating the liquid is negligible as long as the assumption of parallelism of QQ and PP is valid. Equation (43) thus furnishes one boundary condition. The second boundary condition is given by the symmetry. According to this, there is no heat exchanged through the center plane of the plate. This is expressed by

$$\left(\frac{\partial u_1}{\partial x}\right)_{x=0} = 0. \tag{44}$$

Besides the terminal conditions (43) and (44) the differential equation

$$\frac{\partial u_1}{\partial t} = a_1^2\frac{\partial^2 u_1}{\partial x^2}$$

must be fulfilled. This problem has also been solved under the premises defined at the beginning of this article. The details of the exact solution will not be given here as it would occupy considerable space. Only the final result is presented in Fig. 5. "c" is the temperature-time curve at the surface of a plate 2 cm. thick, quenched in ice-water. Curve "*b*" refers to a depth 0.05 cm. below the surface. If, however, the temperature drops slowly, its distribution within the plate must be nearly uniform, which permits solving the problem in an approximate way.

Denote the initial temperature by u_i. Let the heat contained in a prism of 1 cm.^{2} section, extending from the center to the surface, be Q_i. The rate of change of Q_i must be equal to the heat lost per cm.^{2} surface per second, or

$$\frac{dQ}{dt} = K_3\left[\frac{\partial u_3}{\partial x}\right]_{x=0} = -100K_3\frac{1}{a_3\sqrt{\pi t}},$$

$$Q = -100\frac{K_3}{a_3}\frac{2}{\sqrt{\pi}}\sqrt{t} + Q_i,$$

$$Q = uc_1\rho_1 l \qquad Q_i = u_i c_1\rho_1 l.$$

The approximate solution thus is

$$u_i - u = 100\frac{K_3}{a_3c_1\rho_1 l}\frac{2}{\sqrt{\pi}}\sqrt{t}$$

$$= 100\frac{1.4\times10^{-3}}{3.74\times10^{-2}\times0.114\times7.8\times1}\cdot\frac{2}{\sqrt{\pi}}\sqrt{t} = 4.76\sqrt{t}$$

for a plate 2 cm. thick (l = 1 cm.). For comparison this approximate solution is represented by the dotted line "*a*" (Fig. 5) which approaches very closely the accurate solution represented by *C* after a few seconds.

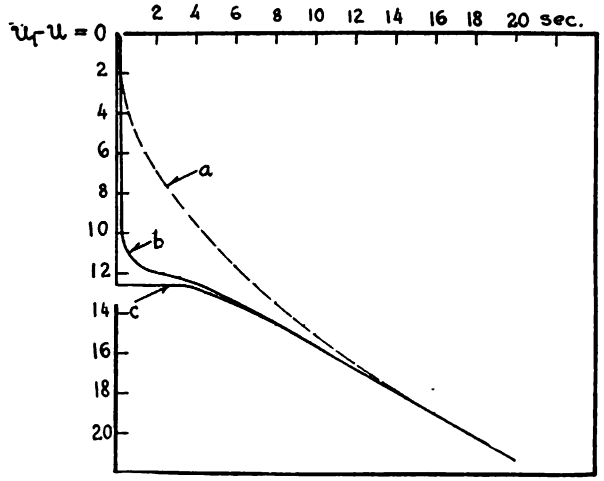

Fig. 5.

IV. Hypothesis 3*b*.

Steam is formed at the boundary of the solid. The surface water-steam remains parallel to the surface of the solid. Heat is removed by convection only, at a uniform rate.

The boundary surface of water-steam *QQ* in Fig. 4 must be at 100° C. Consider the simplest case of uniform turbulence, in which case the rate of removal of heat is constant. Due to the fact that the heat capacity of the steam layer is negligible, the same amount of heat is removed from the metal surface as from the water-steam surface. The amount of heat required to evaporate the liquid must be negligible. (See Hypothesis No. 3*a*.)

Let us assume a plate quenched on both sides. It should be of uniform initial temperature. What will be the temperature at any point of the plate at any time after quenching, if the boundary conditions mentioned above are valid?

$$\frac{\partial u}{\partial t} = a^2 \frac{\partial^2 u}{\partial x^2}, \tag{45}$$

differentiating with respect to *x*,

$$\frac{\partial}{\partial t}\left(\frac{\partial u}{\partial x}\right) = a^2 \frac{\partial^2}{\partial x^2}\left(\frac{\partial u}{\partial x}\right), \tag{46}$$

denote

$$\frac{\partial u}{\partial x} = v, \tag{47}$$

$$\frac{\partial v}{\partial t} = a^2 \frac{\partial^2 v}{\partial x^2}, \tag{48}$$

boundary conditions

$$\text{at center} \left| -K \frac{\partial u}{\partial x} \right|_{x=0} = \left| -Kv \right|_{x=0} = 0, \tag{49}$$

$$\text{at surface} \left| -K \frac{\partial u}{\partial x} \right|_{x=l} = \left| -Kv \right|_{x=l} = C_2 H = \text{constant}, \tag{50}$$

$$t = 0 \quad u = u_i \quad \text{constant within the plate.} \tag{51}$$

Equation (48) has the form of equation (45). The corresponding solution with boundary conditions (49), (50) and (51) is generally known, and may be written

$$v = -\frac{2\pi a^2}{l^2} \sum_{m=1}^{\infty} (-1)^m m \sin\left(\frac{m\pi x}{l}\right) \int_0^t e^{-a^2(m\pi/l)^2(t-\tau)} \frac{C_2}{K} H d\tau, \tag{52}$$

where C_2 designates the temperature at *QQ* above the temperature of the surrounding liquid. We shall assume ice-cold water, in which case $C_2 = 100°$ C.

$$\int_0^t e^{-(am\pi/l)^2(t-\tau)}\,d\tau = \left(\frac{l}{amn}\right)^2 (1 - e^{-(am\pi/l)^2 t}). \tag{53}$$

For abbreviation let us set

$$z = \left(\frac{a\pi}{l}\right)^2 t; \tag{54}$$

then

$$v = \frac{2C_2H}{\pi K}\sum_{m=1}^{\infty}\frac{(-1)^m}{m}\sin\left(\frac{m\pi x}{l}\right)(1 - e^{-m^2 z}). \tag{55}$$

Let the difference of temperature between center and at the point x be Δu_x. From (47)

$$\Delta u_x = \int_0^x \frac{\partial v}{\partial x}dx = \frac{2lC_2H}{\pi^2 K_1}\sum\frac{(-1)^m}{m^2}\left(\cos\left(\frac{m\pi x}{l}\right) - 1\right)(1 - e^{-m^2 z}). \tag{56}$$

In order to be able to determine the drop of temperature at the center below its initial value, equate HC_2t (which is the heat lost through the surface), to the loss of heat in the plate.

$$l\rho c(u_i - u_{x=0}) + c\rho \textstyle\int_0^l \Delta u_x dx = HC_2 t. \tag{57}$$

Substituting the value of Δu_x from (56) in (57), and integrating, the temperature drop at any point of the plate may be expressed by

$$u_i - u_x = \frac{2}{\pi^2} l \frac{H}{K} C_2\left[\sum_{m=1}^{\infty}\frac{(-1)^m}{m^2}\cos\left(\frac{m\pi x}{l}\right)(1 - e^{-m^2 z}) + \frac{z}{2}\right]. \tag{58}$$

The steady state is represented by the linear equation

$$u_1 - u_x = A\frac{z}{2},$$

i.e., the temperature drop is proportional to the time, which is self-evident when considering the premises. Equation (58) is plotted on Fig. 6. The temperature time lines at different depths are parallel.

V. Hypothesis No. 4.

Effect of sudden stop of quenching.

Under No. 3*a* it has been pointed out that a thin soft shell is occasionally found on hard steel articles which were quenched in water. This phenomenon seems to be promoted by warm quenching water and when the quenched pieces touch each other at the bottom of the quenching tank.

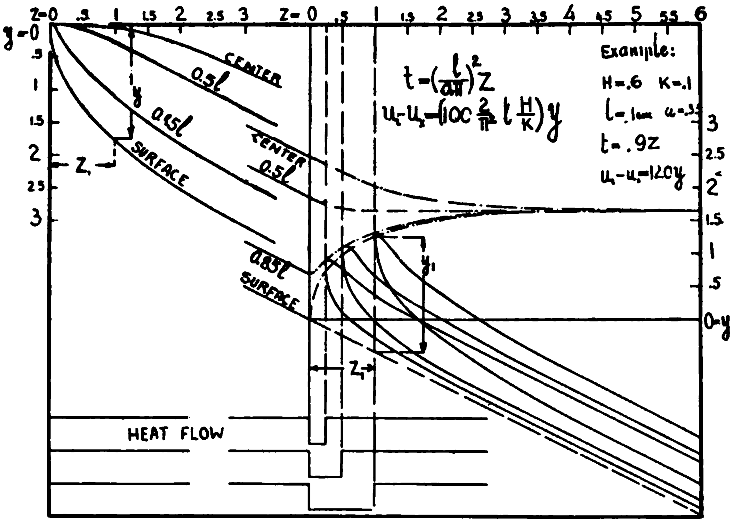

Fig. 6.

It was shown that reheating cannot occur immediately after quenching. All that happens then is a sudden but small drop of temperature to a value which remains constant at the surface untli either the temperature drop reached the center, or the film becomes too thick; the film then collapses and bubbling begins.

The only other explanation of surface reheating is a stop in the flow at a later phase of the cooling process.

According to Portevin, the transformation of structure to hard martensite begins around 300° C. Occasionally microscopic investigations of water-quenched specimens reveal "tempered" needles of martensite at the surface, which postulates the preëxistence of martensite, consequently a temperature of at least 300° C. must have been reached at the surface, after which the temperature must have been raised, so as to produce the tempering.

We shall not enter into speculation about the nature of the obstruction which causes a reheating of the surface, but postulate an ideal case, *i.e.*, an instantaneous and complete arrest of a constant flow of heat. This is a drastic condition but may serve as a point of departure for estimating milder cases.

Let us further suppose that after an arbitrary time limit the obstruction is instantaneously removed and original quenching condition reestablished.

The problem of interrupted heat flow may be solved in a simple way when considering that the underlying differential equation is a linear one, with constant coefficients. This equation is satisfied by the sum of any number of particular solutions. The physical interpretation of this fact is the principle of superposition, *i.e.*, the coexistence of different flows without mutual disturbance. The resultant flow is the sum of the components.

This principle may be applied with advantage to the present problem. The solution may result from two heat currents in opposite direction, and the fictitious influx would set in at the time when the arrest of the influx in the original problem begins. According to the principle of superposition the two currents, equal and opposite, counteract each other, the result being a stop of flow. The graphical construction is thus as follows: The temperature-curve which corresponds to a *constant* outflux of heat at the surface is first plotted (Equation (58)). The moment of arrest of heat on the time scale is then marked, and regarded as a second origin. The drop in the first system (say y_1, in Fig. 6) at a given time (z_1), is added to the system defined by the second origin as indicated in Fig. 6.

Fig. 6 is drawn on a general scale, which may be specialized to given constants. This is shown in an example. $H = 0.6$ g. cal. cm.$^{-2}$ sec.$^{-1}$ C.$^{\circ -1}$ is assumed, which is the highest value computed in the following article. From Fig. 6 it is obvious that an increase in the intensity of quenching (H) increases the maximum temperature rise in reheating. At $0.85l$ (1.5 mm. depth on a 2 cm. plate) the maximum reheating would be considerably less (about 57 per cent. of the surface). The decrease of the relative maximum reheating does not depend on the quenching speed if the premises of our deductions are valid. An overheating at any point closer than 0.5 to the center is not possible under the assumed cooling law.

To be able to form an idea about the magnitude of reheating, let us assume an example.

For $H = 0.6$ g. cal. cm.$^{-2}$ sec.$^{-1}$ C.$^{\circ -1}$; $l = 1$ cm. (thickness of plate = 2 cm.);

$$K = .1 \text{ g. cal. cm.}^{-1} \text{ sec.}^{-1} \text{ C.}^{\circ -1}; \qquad a = 0.33 \text{ cm. sec.}^{-1/2}.$$

The increase of temperature after a stop lasting for 0.45 second, is 120° C. at the surface and 48° at a depth of 1.5 mm. In 0.9 second this would increase to 150° C. and 72° C. respectively. With an arrest of flow for an indefinite time, the temperature rise would be 200° C. at the surface.

VI. DISCUSSION OF THE RESULTS AND COMPARISON WITH TEST DATA.

In the foregoing articles four cooling hypotheses were examined, each one leading to a solution characteristic of the surface cooling. In every case it was assumed that the constants of the metal do not vary with the temperature and no heat was liberated within the metal during quenching. The results derived in the first two cases are exponential functions, *i.e.*, the steady state appears as a straight line if time is plotted to a uniform scale and the corresponding temperature to a logarithmic scale. In the third case the steady state is a parabolic curve, *i.e.*, straight on a double logarithmic paper. In the fourth case the relation between time and temperature is linear.

Experimental cooling curves by Portevin[2] on water quenching of cylinders are plotted on semi-logarithmic paper. Also curves for Ni Si cylinder by Pilling and Lynch[3] and for steel cylinder by Honda[4] are plotted for comparison. (Fig. 7.) The abscissa were shifted in some cases to avoid the starting condition, *i.e.*, before steady state was reached.

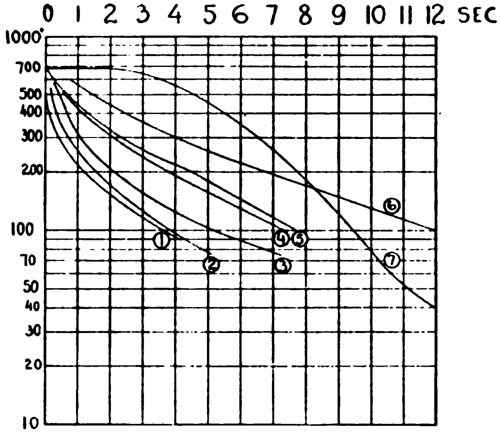

Fig. 7.

1. Silver cylinder 0.8 cm. dia. × 2.4 cm. long, quenched in running tap water, by Portevin and Garvin.

2. Silver cylinder 1.2 cm. dia. × 3.6 cm. long, quenched in running rap water, by P. and G.

3. Silver cylinder 2 cm. dia. × 6 cm. long, quenched in running tap water, by P. and G.

4. Nickel cylinder 1.2 cm. dia. × 3.6 cm. long, quenched in running tap water, by P. and G.

5. 95 per cent. Ni + 5 per cent. Si; cylinder 0.64 cm. dia. 5 cm. long, quenched in water or 1° C., by Pilling and Lynch.

6. Nickel cylinder 2 cm. dia. × 6 cm. long, quenched in running tap water, by Portevin and Garvin.

7. Steel cylinder 1.26 per cent. C, 2 cm. dia. × 2 cm. long, quenched in water, by Honda.

None of the curves are straight lines at high temperatures. The heavier pieces show an almost straight course at a later phase of cooling. This indicates that the surface soon reaches the constant temperature as per Article I. In other words, the larger the mass, or lower the conductivity, the more accurately will the hypothesis of instantaneous surface cooling apply, when points in the vicinity of the center are considered.

The fact that at higher temperatures the experimental curves do not appear as straight lines, if plotted on semi-logarithmic paper, is a proof that Newton's cooling constant depends on the surface temperature. For a short interval it is legitimate to regard H constant, and it is possible to determine its approximate value from the curves obtained by experiment. The determination is the more accurate the smaller the difference of temperature between surface and center. In this case the conception of steady flow may be maintained, which would be expressed by the fact that the temperature-time-space equation may be reduced to the first member of the series.

For the cylinder (Equation 17)

$$u = a_1 b_1 J_0(\rho\lambda_1) \cos(z\rho_1) e^{-a^2(\lambda_1^2+p_1^2)t}. \tag{59}$$

$$\text{Set } a^2(\lambda_1^2 + p_1^2) = m. \tag{60}$$

Take the logarithm of both members of the equation (59)

$$\log_{10} u = \log_{10}(a_1 b_1 J_0(\rho\lambda_1) \cos(zp_1)) - mt \log_{10} e.$$

This equation appears as a straight line on semi-logarithmic paper, $-mt$ being the slope of the line. By drawing tangents to the experimental cooling curve, it is possible to determine the instantaneous values of m. Thus equations (15), (16) and (60) contain three unknown quantities λ_1, p_1 and h, which may be determined. $H = Kh$ by definition.

The surface temperature which corresponds to the instantaneous value of H, at a given center temperature, may be determined from equation

$$\frac{u_s}{u_c} = \frac{J_0(R\lambda_1)}{J_0(0)} = J_0(R\lambda_1). \tag{59}$$

The value of H has been derived from three of the experimental curves shown in Fig. 7.

Curves No. 1 and No. 3 refer to 0.8 cm. dia. × 2.4 cm. long and 2 cm. × 6 cm. silver cylinders respectively. Curve No. 5 shows cooling of a 0.64 × 5 cm. cylinder consisting of 95 per cent. N; and 5 per cent. Si. The good heat conductivity of the former and the small diameter of the latter specimen may justify the assumption of "steady flow," when determining H. The greatest temperature drops between center and surface are: 8 per cent., 24 per cent., and 10 per cent. respectively.

In Fig. 8 values of H are plotted against the surface temperature on semi-logarithmic paper. From this it appears that at higher temperatures H is an exponential function of the temperature, thus it is far from being constant. This is also borne out by a preliminary experiment made on electrically heated wire submerged in petroleum.

The absolute size of the specimen also seems to have an influence on the magnitude of H. The smaller the specimen, the smaller H seems to be.

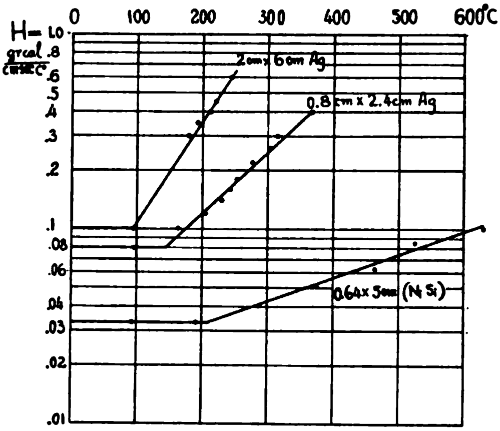

Fig. 8.

Comparison of the experimental curves with solutions obtained in Article 3*a* and 3*b* bears out the fact that Hypothesis 3*a* is untenable after the first stage of quenching. It results in a too slow cooling as compared with experiment. The fact that the experimental curves are not straight lines as shown in the articles by Portevin, Honda and Pilling, is a proof that neither is Hypothesis 3*b* valid. This may be explained by the fact that the thickness of the steam film grows rapidly (Fig. 9),

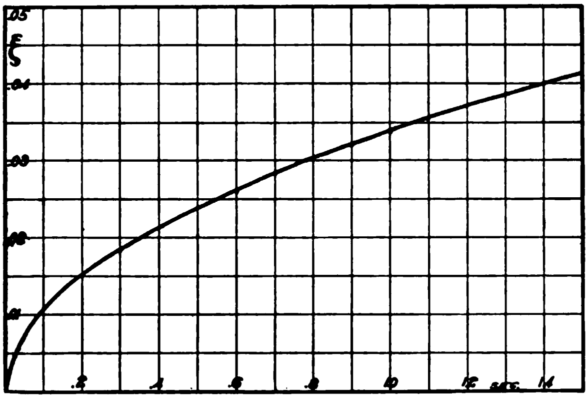

Fig. 9.

becomes unstable and bubbling sets in, which renders a mathematical treatment difficult. That bubbling sets in is also indicated by the vibration, which is transmitted by the liquid to the surface of the tank, where it may be felt.

CONCLUSIONS.

1. It has been shown that it is possible to calculate the temperature in the vicinity of the center but not at the surface of a regularly shaped body, provided the body is large, or it is a poor conductor of heat. In such cases the substitution of water in place of oil does not improve the quenching speed at the center.

2. An increase of quenching temperature results in increased quenching speed at a given lower temperature. This is important in the practice of hardening of steel. It is impossible to obtain good hardness if the specimen is quenched at a temperature just above the critical.

3. Newton's cooling law may also be interpreted as a constant surface resistance (scale) obstructing emission of heat.

4. A very rapid cooling of the surface to low temperatures in quenching media similar to water, with immediate reheating due to formation of a steam jacket, is not possible. The surface temperature drops instantaneously by an insignificant amount, which is followed by a gradual drop.

5. Assuming a constant rate of heat emission, which is suddenly stopped, a reheating of the surface is possible. The amount of reheating is the greater the swifter the drop preceding the arrest of flow. Reheating cannot occur at the vicinity of the center.

6. The specific surface emission is not proportional to the surface temperature, but Newton's "constant" increases exponentially with the temperature. It seems also to depend on the absolute size of the quenched object, smaller sizes having smaller specific emission. This would point to a difficulty in obtaining very great quenching speeds by trying to reduce the diameter of the quenched specimen.

In conclusion, I wish to acknowledge my appreciation to S K F Research Laboratory and particularly to Dr. Styri, for originally suggesting this work, and to S K F Industries, Inc., New York, for granting the opportunity to complete this investigation.

I am also indebted to the following members of the S K F Laboratory for their valuable assistance in preparing this paper: Messrs. H. Sjövall, W. F. Titus, and H. O. Walp.

THE STRESS-ENERGY TENSOR IN ELECTROMAGNETIC THEORY AND A NEW LAW OF FORCE.

By H. Bateman.

Synopsis.

Modified Electromagnetic Theory.—By suitably modifying the equations for the components of the stress-energy tensor it is possible to reconcile electromagnetic theory with the idea of non-radiating electronic orbits. The change, however, is equivalent to assuming that an element of electricity is acted upon by a *new force* which depends on the gradient of the density of electricity and balances the usual electromagnetic force. By assuming a certain *distribution of density within an electron* it is also possible to account for the existence of discrete electronic charges.

1. *The Stress-energy Tensor.*—We shall assume that the stress-energy tensor associated with a system of electric charges has the following components:

$$W = \tfrac{1}{2}(E^2 + H^2) + \frac{2}{c^2}\psi\frac{\partial^2\psi}{\partial t^2} + \left(\frac{\partial\psi}{\partial x}\right)^2 + \left(\frac{\partial\psi}{\partial y}\right)^2 + \left(\frac{\partial\psi}{\partial z}\right)^2 - \frac{1}{c^2}\left(\frac{\partial\psi}{\partial t}\right)^2;$$

$$S_x = c[E_yH_z - E_zH_y] - 2\psi\frac{\partial^2\psi}{\partial x\partial t}, \qquad \text{etc.};$$

$$X_x = \tfrac{1}{2}[E_x^2 - E_y^2 - E_z^2 + H_x^2 - H_y^2 - H_z^2]$$
$$- 2\psi\frac{\partial^2\psi}{\partial x^2} + \left(\frac{\partial\psi}{\partial x}\right)^2 + \left(\frac{\partial\psi}{\partial y}\right)^2 + \left(\frac{\partial\psi}{\partial z}\right)^2 - \frac{1}{c^2}\left(\frac{\partial\psi}{\partial t}\right)^2;$$

. . . .

$$Y_x = X_y = E_xE_y + H_xH_y - 2\psi\frac{\partial^2\psi}{\partial x\partial y}, \qquad \text{etc.}$$

The quantity W represents the density of energy, the vector S specifies the flow of energy and is proportional to the density of momentum; the six quantities X_x, Y_y, Z_z, Y_z, Z_x, X_y are the components of stress; v is the velocity of electricity at a point (ξ, η, ζ) where the density of electricity at time τ is ρ; E and H are the field vectors in the electromagnetic field produced by the electric charges and ψ is a retarded potential defined by the equations

$$\psi = \frac{1}{4\pi}\int\frac{d\xi d\eta d\zeta}{r}\left[\rho\sqrt{1 - \frac{v^2}{c^2}}\right],$$

$$r^2 = (x - \xi)^2 + (y - \eta)^2 + (z - \zeta)^2 = c^2(t - \tau)^2, \qquad \tau < t,$$

c being the velocity of light.

The components of the total force F are given by the three equations of type

$$F_x = \frac{\partial X_x}{\partial x} + \frac{\partial Y_x}{\partial y} + \frac{\partial Z_x}{\partial z} - \frac{1}{c^2}\frac{\partial S_x}{\partial t}$$

and we find that

$$F_x = \rho\left[E_x + \frac{1}{c}(v_yH_z - v_zH_y)\right] - 2\psi\frac{\partial}{\partial x}\left[\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} - \frac{1}{c^2}\frac{\partial^2\psi}{\partial t^2}\right]$$

$$= \rho\left[E_x + \frac{1}{c}(v_yH_z - v_zH_y)\right] + 2\psi\frac{\partial}{\partial x}\left[\rho\sqrt{1 - \frac{v^2}{c^2}}\right].$$

The energy equation

$$\frac{\partial S_x}{\partial x} + \frac{\partial S_y}{\partial y} + \frac{\partial S_z}{\partial z} + \frac{\partial W}{\partial t} = -(v\cdot F)$$

requires that

$$\psi\frac{d}{dt}\left[\rho\sqrt{1 - \frac{v^2}{c^2}}\right] = 0,$$

where

$$\frac{d}{dt} = \frac{\partial}{\partial t} + v_x\frac{\partial}{\partial x} + v_y\frac{\partial}{\partial y} + v_z\frac{\partial}{\partial z}.$$

It seems reasonable to adopt the hypothesis that F is everywhere zero.

2. *The Existence of Discrete Charges.*—When all the electric charges are stationary ψ becomes the electrostatic potential and

$$F_x = -\rho\frac{\partial\psi}{\partial x} + 2\psi\frac{\partial\rho}{\partial x}.$$

consequently F vanishes everywhere if

$$\rho\frac{\partial\psi}{\partial x} = 2\psi\frac{\partial\rho}{\partial x},$$

$$\rho\frac{\partial\psi}{\partial y} = 2\psi\frac{\partial\rho}{\partial y},$$

$$\rho\frac{\partial\psi}{\partial z} = 2\psi\frac{\partial\rho}{\partial z},$$

and this means that

$$\psi = b^2\rho^2,$$

where b^2 is a constant. The function ψ then satisfies the partial differential equation

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{1}{b}\sqrt{\psi} = 0.$$

Let us consider the case in which ρ is a function of the radius r from a point o and differs from zero only within a sphere of radius a. Assuming that

$$\rho = A_0 + A_2\left(\frac{r}{a}\right)^2 + A_4\left(\frac{r}{a}\right)^4 + \cdots,$$

we find that

$$\psi = \frac{1}{3\cdot 2}(3a^2 - r^2)A_0 + \frac{1}{4\cdot 5}\left(5a^2 - \frac{r^4}{a^2}\right)A_2 + \frac{1}{6\cdot 7}\left(7a^2 - \frac{r^6}{a^4}\right)A_4 + \cdots;$$

consequently

$$b^2\left[A_0 + A_2\left(\frac{r}{a}\right)^2 + A_4\left(\frac{r}{a}\right)^4 + \cdots\right]^2 = \frac{1}{2\cdot 3}(3a^2 - r^2)A_0 + \frac{1}{4\cdot 5}\left(5a^2 - \frac{r^4}{a^2}\right)A_2 + \cdots.$$

Equating coefficients we find that

$$\rho = A_0\left[1 - \frac{1}{12}\frac{r^2}{A_0b^2} - \frac{1}{720}\frac{r^4}{A_0{}^2b^4} - \frac{1}{10080}\frac{r^6}{A_0{}^3b^6} - \frac{31}{6!\,7!}\frac{r^8}{A_0{}^4b^8} - \frac{(971)(24)}{(6!)(11!)}\frac{r^{10}}{A_0{}^5b^{10}} - \cdots\right],$$

$$f(\xi) \equiv 1 - \frac{1}{2}\xi + \frac{1}{48}\xi^2 + \frac{1}{4320}\xi^3 + \frac{1}{80640}\xi^4 + \frac{31}{(10)(6!)(7!)}\xi^5 + \frac{(971)(24)}{(6!)(12!)}\xi^6 + \cdots.$$

The equation $f(\xi) = 0$ has two roots, one of which is approximately $2\cdot 2$; the second is difficult to determine accurately as it is necessary to consider a large number of terms of the series; it appears to lie between 12 and 6 and is probably about 11.

When a and the total charge e are given, A_0 and b are determined, but there are two possible solutions and so there are two different types of discrete charge.[1] The present analysis does not, however, indicate the size of the electron.

[1] It is interesting to compare the solution of the equation $\psi = b^2\rho^2$ with that of the simpler equation $\psi = b^2\rho$ which would also lead to discrete charges. In the latter case we may have

$$\psi = \frac{1}{r}\sin\left(\frac{r}{b}\right) = b^2\rho,$$

the radius of the sphere being determined by the equation $a = b\pi(n + \frac{1}{2})$, where n is an integer. We have in fact

$$\psi = \int_r^a \rho r dr + \frac{1}{r}\int_0^r \rho r^2 dr = \frac{1}{b^2}\int_r^a \sin\left(\frac{r}{b}\right)dr + \frac{1}{b^2r}\int_0^r \sin\left(\frac{r}{b}\right)r dr = \frac{1}{r}\sin\left(\frac{r}{b}\right)\cdot$$

The total electric charge is then

$$e = \int_0^a \rho r^2 dr = \sin(n + \tfrac{1}{2})\pi = (-1)^n$$

3 *The Radiation of Energy from a Moving Electric Pole.*—In the case of a moving point charge of electricity we must put

$$\psi = -\frac{e}{4\pi M}\sqrt{c^2 - \xi'^2 - \eta'^2 - \zeta'^2} = -\frac{e}{4\pi M}\sqrt{c^2 - v^2},$$

where $\xi(\tau)$, $\eta(\tau)$, $\zeta(\tau)$ are the coördinates of the charge e at time τ and M is defined as a function of x, y, z, t by the equations

$$M = [x - \xi(\tau)]\xi'(\tau) + [y - \eta(\tau)]\eta'(\tau) + [z - \zeta(\tau)]\zeta'(\tau) - c^2(t - \tau)$$
$$[x - \xi(\tau)]^2 + [y - \eta(\tau)]^2 + [z - \zeta(\tau)]^2 = c^2(t - \tau)^2$$
$$\tau < t.$$

Calculating S_x and retaining only terms of order $1/M^2$ we have

$$S_x \sim \frac{e^2c^2(t - \tau)(x - \xi)}{16\pi^2 M^4}\left[\left\{v'^2 - 2(vv')\frac{K}{M} - (c^2 - v^2)\frac{K^2}{M^2}\right\}\right.$$
$$\left. + 6(vv')\frac{K}{M} + 6(c^2 - v^2)\frac{K^2}{M^2} - 2v'^2 - \frac{2(vv')^2}{c^2 - v^2} - 2(vv'') - \frac{2L}{M}(c^2 - v^2)\right],$$

where

$$K = (x - \xi)\xi'' + (y - \eta)\eta'' + (z - \zeta)\zeta'',$$
$$L = (x - \xi)\xi''' + (y - \eta)\eta''' + (z - \zeta)\zeta'''.$$

To calculate the radiation we must first of all replace $(x - \xi)$ in S_x by $c(t - \tau)$ to get the radial component of S. We must next multiply by a Doppler factor and this[1] is equivalent to replacing $(x - \xi)$ in S_x by $-M/c$. The final step is to integrate over a large sphere whose center is at the pole. Writing

$$I_n^m = \int_0^\pi \frac{\cos^m\theta \sin\theta d\theta}{(c - v\cos\theta)^n}$$

we have

$$I_3^0 = \frac{2c}{(c^2 - v^2)^2}, \qquad I_4^1 = \frac{8cv}{3(c^2 - v^2)^3},$$

$$I_5^0 = \frac{2c(c^2 + v^2)}{(c^2 - v^2)^4}, \qquad I_5^2 = \frac{2c(c^2 + 5v^2)}{3(c^2 - v^2)^4},$$

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and there is a different type of discrete charge for each positive integral value of n. In this case ρ is determined by a homogeneous linear integral equation while in the other case the integral equation is not linear. The equation $\psi = b^2\rho$ is used by A. Korn in his mechanical theory of the electromagnetic field. Phys. Zeitschr., Bd. 19 (1918), p. 234. Another distribution of density is considered by G. Mie, Ann. d. Phys., Bd. 39 (1912), p. 1.

[1] Cf. M. Abraham, Theorie der Elektrizität, Bd. II., p. 108. A Liénard, L'éclairage électrique (1898).

and we find that the rate of radiation is

$$R = \frac{e^2}{6\pi c^3}\left[\frac{\dot{v}^2 + (v\ddot{v})}{(c^2 - v^2)^2} + \frac{4(v\dot{v})^2}{(c^2 - v^2)^3}\right]$$

$$= \frac{e^2}{6\pi c^3}\frac{d}{d\tau}\left[\frac{(v\dot{v})}{(c^2 - v^2)^2}\right] = \frac{e^2}{12\pi c^3}\frac{d^2}{d\tau^2}\left[\frac{1}{c^2 - v^2}\right].$$

In a periodic motion the integral

$$\int R d\tau$$

taken over a complete period is zero and so there is no radiation of energy to infinity on the average.

It may be remarked that there is no radiation of energy to infinity when the components of the stress-energy tensor are given by[1]

$$W = \left(\frac{\partial\psi}{\partial x}\right)^2 + \left(\frac{\partial\psi}{\partial y}\right)^2 + \left(\frac{\partial\psi}{\partial z}\right)^2 + \frac{1}{c^2}\left(\frac{\partial\psi}{\partial t}\right)^2 - \frac{1}{2}(E^2 + H^2),$$

$$S_x = -2\frac{\partial\psi}{\partial t}\frac{\partial\psi}{\partial x} - c(E_y H_z - E_z H_y),$$

$$X_x = -\left(\frac{\partial\psi}{\partial x}\right)^2 + \left(\frac{\partial\psi}{\partial y}\right)^2 + \left(\frac{\partial\psi}{\partial z}\right)^2 + \frac{1}{c^2}\left(\frac{\partial\psi}{\partial t}\right)^2$$

$$- \frac{1}{2}(E_x^2 - E_y^2 - E_z^2) - \frac{1}{2}(H_x^2 - H_y^2 - H_z^2),$$

$$X_y = Y_x = -2\frac{\partial\psi}{\partial x}\frac{\partial\psi}{\partial y} - E_x E_y - H_x H_y,$$

but in this case the force is

$$F_x = 2\rho\sqrt{1 - \frac{v^2}{c^2}}\frac{\partial\psi}{\partial x} - \rho\left[E_x + \frac{1}{c}(v_y H_z - v_z H_y)\right]$$

and cannot be made to vanish at each point.

The present analysis does not lead to quantum theory because the electron has been treated as a point charge. It looks as if certain conditions may have to be satisfied in order that F may vanish everywhere when an electron of finite size describes an orbit round a positive nucleus. A discussion of this problem with the aid of the equations of § 1 looks difficult and will not be attempted here.

California Institute of Technology, Pasadena,
April 10, 1922.

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[1] The expressions depending on ψ are similar to those used by Volterra, Abraham and McLaren in the theory of gravitation. V. Volterra, Il Nuovo Cimento (1899), p. 337; M. Abraham, Phys Zeitschr. (1912), p. 1; S. B. McLaren, Phil. Mag., Oct., 1913, p. 635.

NOTE, ADDED JUNE 9, 1922.

It may be shown also that, when a point charge of electricity moves with an arbitrary velocity less than c, the rate at which linear momentum is radiated to infinity is the time derivative of a uniform function of the velocity and acceleration of the point charge. There is no radiation of momentum in a certain interval of time if the velocity and acceleration have the same values at the beginning and end of the interval.

With the new stress-energy tensor there appears also to be no radiation to infinity of angular momentum in the field of a Hertzian dipole.

Negative values of W may be avoided by introducing an additional stress-energy tensor corresponding to a universal constant negative pressure.

THE VARIATION OF THE INDEX OF REFRACTION OF WATER, ETHYL ALCOHOL, AND CARBON BISULPHIDE, WITH THE TEMPERATURE.

By Elmer E. Hall and Arthur R. Payne.

Synopsis.

Index of Refraction of Pure Water for Sodium Light from 15° to 100° C.—Very few observations had previously been made for temperatures above 50° C. A precision spectrometer was used. The brass prism with optical glass windows was gold plated inside to prevent contamination of the pure gas-free water tested, and means were provided for keeping the temperature within 0.1° C. Many readings were taken and the average values are probably accurate to within about 0.00002. When reduced to vacuum they are well represented by the empirical formula: $n = 1.33401 - 10^{-7}(66t + 26.2t^2 - 0.1817t^3 + 0.000755t^4)$. The *temperature coefficient* dn/dt changes from $-8(10)^{-5}$ at 15° to $-30(10)^{-5}$ at 100°.

Index of Refraction of Commercially Pure Ethyl Alcohol and Carbon Bisulphide for Sodium Light from 15° up to the Boiling Points.—While Kahlbaum's ethyl alcohol, 99.8 per cent. absolute, and Baker's C.P. CS_2 were used, the absolute values obtained differ somewhat from those given by others for pure samples. Nevertheless the *temperature coefficients* are probably not affected by the slight amount of impurity present and are of interest because very few results are available for liquids at temperatures above 40° C. The results correspond to the empirical equations: $dn/dt(\text{ethyl alcohol, } 15 \text{ to } 70^\circ) = -10^{-6}[404 + 0.44(t - 15) + 0.0075(t - 15)^2]$; $dn/dt(CS_2, 15 \text{ to } 45^\circ) = -10^{-6}[766 + 5.12(t - 15) - 0.105(t - 15)^2]$.

Introduction.—Historically the study of the change in the index of refraction of liquids with change in temperature dates from the work of Jamin in 1856.[1] Most of the investigations made have been at temperatures not differing greatly from room temperature. In the case of water all the investigations, with two exceptions, are within the temperature range of 0° to 50° C. The two exceptions mentioned are the work of Ruhlman[2] and Kettler,[3] whose investigations included temperatures in the range 50 to 100° C. A partial bibliography for the three liquids mentioned in the title may be found in Landolt-Bornstein Tabellen. A brief incomplete historical summary for the case of water is given by Osborn.[4] Osborn's work is concerned only with the change in the index of refraction of water with the temperature, the absolute value of the index not being determined. For the range 1° to 38° C. he determined this change to approximately one unit in the seventh decimal place.

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[1] Comptes Rendus, 43, 1191, 1856.

[2] Pogg. Ann., 132, 177, 1867.

[3] Ann. d. Phys., 33, 353 and 506, 1888.

[4] Phys. Rev., 2d series, 1, 198, 1913.

This work, together with the value of the index as found in such investigations as those of Walter,[1] Gifford[2] and Baxter, Burgess, and Daudt,[3] constitutes a very complete study for the range below 40° C. The data for the range above 40° seem to be somewhat uncertain, the work of Ruhlman and Kettler not being always in good agreement. It therefore seemed justifiable to the writers to study anew the index of refraction of water, especially in the region between 40° and 100° but making a sufficient number of determinations below 40° to enable a comparison to be made with other recent determinations. Determinations of the index of refraction of ethyl alcohol and carbon bisulphide from 15° C. to their boiling points are also included.

Apparatus and Method.—After preliminary trials of different methods, the spectrometer method was adopted. There was available a new precision spectrometer, designed by one of the writers, and built in the shop of the department of physics. The weight of the heavy telescope, counterpoise, and table was supported in part by ball bearings, the design thus permitting of a fairly heavy load on the spectrometer table. The instrument was provided with all needed slow motions, clamping devices and adjustments. The ten-inch circle, divided into one twelfth degrees, was cut on the automatic circular dividing engine which was also built in the shop of the department of physics.[4] By the use of two microscopes with travelling eyepieces, 180° apart, the scale could be read to one half seconds if desired. The circle was cut soon after the calibration of the dividing engine, and the engine and circle showed errors not exceeding eight seconds. It was found that errors of setting were slightly greater than errors of graduation. With the first prism described below readings were made for each temperature on different parts of the scale, attempting thereby to eliminate errors of graduation by using different parts of the scale. Errors in setting were cared for by taking the mean of a large number of settings. With the second prism described below a calibrated part of the scale was used.

Two different prisms and heating devices were used. In the first of these, used for water only, the prism had a refracting angle of approximately 75°. It was constructed of heavy brass, with optical glass plates clamped on the sides. These plates were carefully tested. The faces of the brass prism were first milled as true as possible and then ground down and polished with abrasive powder and rouge. The glass plates were placed directly against the polished brass. The cubical contents of the prism were 70 c.c. The water was kept well stirred by an electrically driven stirrer. The stirrer and the interior of the brass prism were heavily gold plated. It was found that enough brass would dissolve in the water in the course of a few hours to change the index of refraction by approximately two units in the fourth decimal place. The prism was placed inside a double-walled, jacketed and well-insulated, electrical heating device. This jacketed heater, which measured 17 cm. in diameter by 12 cm. high, was placed on the spectrometer table from which it was well insulated. The jacket was provided with sliding shutters over the windows of the prism, these shutters being kept closed except when a reading was being made. It was found that the temperature could be brought readily to any desired point and held there ndefinitely to within one tenth of a degree. The temperature was measured with a calibrated Baudin mercury thermometer placed close to the line of vision. As a check, and also to determine the uniformity of the temperature distribution within the water, two thermocouples were inserted, the galvanometer used being sensitive enough to detect changes of 0.1°.

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[1] Ann. d. Phys., 46, 423, 1892.

[2] Roy. Soc. Proc., 78, 406, 1906.

[3] Am. Chem. Soc. Jr., 33, 1, 893, 1911.

[4] PHYS. REV., XXX., 492, 1910.

In the second form of apparatus the prism, again of brass, gold plated, with optical glass sides, had an angle of approximately 60° and was surrounded, except over the windows, by an oil-bath heater. The oil was heated electrically in a forty-gallon tank and by a rotary pump made to circulate vigorously about the prism. The heaters within the tank were operated by a thermostat and the temperature control rendered automatic. The main advantage in this form of heater was in the time saved through the automatic control. The temperature remained constant to within one twentieth of a degree during the time of making a set of readings at any temperature. In this case the thermometer was nearly totally immersed, thus obviating the necessity of stem corrections. The cubical contents of this prism were about 1500 c.c. The prism angle was of course redetermined for each prism every time the prism was cleaned, and the value checked to be sure that it did not change with change in temperature during a set of measurements.

Purity of the Water.—Since very small amounts of impurities were found materially to change the index of refraction special care was taken to obtain chemically pure water. This was furnished by the chemistry department and was redistilled in block tin and condensed directly into "Resistenz" bottles. In this way it was kept practically free from gases and no impurities could be detected. The conductivity was not taken. The usual method of heating to the boiling point was used to keep the liquid gas-free during a set of readings. After gold plating the interior of the prism contamination during use was practically eliminated. At a given temperature the water was often poured out, the prism washed and refilled and brought to the temperature under investigation with no change in the results.

Accuracy.—The index was calculated from the common minimum deviation formula. In determining the angle of minimum deviation the double angle was usually measured, that is, the prism was reversed and readings to the right and left of the zero setting taken. Six or seven readings were taken for each setting and with the first type of prism used these were repeated for different parts of the scale with the water held at a particular temperature. Readings taken throughout the temperature range were repeated during a period of several months and hence the values given represent the mean of a large number of readings. In determining the angle of the prism and the angle of minimum deviation the individual readings rarely differed from the mean by more than ten seconds and in most cases by much less than this amount. An error of ten seconds in the angle of minimum deviation introduced an error of approximately 3 units in the fifth decimal place with the 75° prism and 4 units in the fifth place with the 60° prism. An error of ten seconds in determining the angle of the prism introduced an error of approximately 2 units in the fifth place. It is believed that the final values for water relative to air given in Table II. are correct to within 2 units in the fifth place throughout the lower temperature range and to within 3 units in the fifth place for the higher temperature range. In Table IV. the values are reduced to the absolute index of refraction in order to compare them with the results of Kettler. In reducing the values observed in air to absolute values the question of distribution of the temperature gradient in the air outside the prism enters. Baxter, Burgess, and Daudt,[1] and others, have multiplied the value obtained in air by the index of refraction of air at the temperature of the water. Where the prism method is used this virtually assumes that the surfaces of equal temperature in the air outside the prism are normal to the direction of the incident and the emergent light. It is believed by the writers that with the prism used by them the more reasonable assumption is that the surfaces of equal temperature outside the prism are parallel to the faces of the prism, in which case it is the index of refraction of the air at room temperature which enters, irrespective of the temperature of the water in the prism. Hence in reducing the values to the absolute index the value obtained in air was, in each case, multiplied by 1.000272, the index of refraction of air at 20° C., which was approximately the room temperature throughout the investigation. At the highest temperature used the difference in the absolute index obtained by using the index of air at the room temperature and by using the index of air at the temperature of the water amounts to 8 units in the fifth place. Close to the prism faces the assumption made by the writers is doubtless nearest the truth; as one recedes from the prism faces, especially beyond the insulating jacket, the first assumption named more nearly represents the truth. The correct value therefore lies somewhere between the two. Of the two assumptions, if the one made by the writers be given the greater weight, then the error introduced by the uncertainty of the distribution of the temperature gradient in the air outside the prism cannot exceed 4 units in the fifth place at the highest temperature used. Hence the values of the index of refraction of water relative to vacuum are believed to be correct to within 2 units in the fifth place at approximately room temperatures, the possible error increasing with rise of temperature to perhaps three times this value at 100°. Changes in the index of refraction of air due to barometric changes affected the results by less than one unit in the fifth decimal place and were disregarded.

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[1] Loc. cit.

Results for Water.—In computing the observations for water where the actual temperatures differed by only a few tenths of a degree from integral values, the results were reduced to those for integral temperatures by interpolation. With this modification Table I. gives the experimental values obtained for the index of refraction of pure water relative to air for sodium light.

Table I.

The Index of Refraction of Pure, Gas-free Water, Relative to Air, for Sodium Light.

Temperature.	Index.	Temperature.	Index.	Temperature.	Index.	Temperature.	Index.
16° C....	1.33333	30° C...	1.33190	60° C...	1.32716	85° C...	1.32172
17......	1.33325	40......	1.33049	62......	1.32678	87......	1.32123
18......	1.33317	44......	1.32992	65......	1.32616	90......	1.32042
19......	1.33308	48......	1.32928	70......	1.32510	93......	1.31973
20......	1.33298	50......	1.32894	73......	1.32444	95......	1.31922
22......	1.33284	52......	1.32858	77......	1.32354	97......	1.31878
24......	1.33262	55......	1.32807	80......	1.32284	98.4....	1.31828
26......	1.33241	56......	1.32799	81......	1.32259		
28......	1.33220	58......	1.32758	82.5....	1.32218		

A large scale plot was made of the above values from which the values given in Tables II. and III. are taken.

In Tables III. and IV. the writers' values are compared with those of other observers. Table IV. is obtained from Table II. by multiplying

TABLE II.

The Index of Refraction of Pure Water, Relative to Air, for Sodium Light, obtained by Plotting the Results Given in Table I.

Temperature.	Index.	Temperature.	Index.	Temperature.	Index.	Temperature.	Index.
15° C....	1.33341	38° C...	1.33079	62° C...	1.32678	86° C..	1.32148
16......	1.33333	40......	1.33051	64......	1.32636	88.....	1.32100
18......	1.33317	42......	1.33023	66......	1.32596	90.....	1.32050
20......	1.33299	44......	1.32992	68......	1.32555	92.....	1.32000
22......	1.33281	46......	1.32959	70......	1.32511	94.....	1.31949
24......	1.33262	48......	1.32927	72......	1.32466	96.....	1.31897
26......	1.33241	50......	1.32894	74......	1.32421	98.....	1.31842
28......	1.33219	52......	1.32860	76......	1.32376	99.....	1.31813
30......	1.33192	54......	1.32827	78......	1.32332	100.....	1.31783
32......	1.33164	56......	1.32792	80......	1.32287		
34......	1.33136	58......	1.32755	82......	1.32241		
36......	1.33107	60......	1.32718	84......	1.32195		

by 1.000272, the refractive index of air. A column giving the variation of the index of refraction with the temperature is included in Table IV.

TABLE III.

Index of Refraction of Water, Relative to Air, Sodium Light.

Temperature.	Hall-Payne.	Walter.	Baxter-Burgess-Daudt.	Gifford.
15° C.........	1.33341	1.33339		1.33343
16............	1.33333	1.33331		
18............	1.33316	1.33316		
20............	1.33299	1.33299	1.33299	
22............	1.33281	1.33281		
24............	1.33262	1.33261		
25............	1.33251	1.33251	1.33248	
26............	1.33241	1.33240		
28............	1.33219	1.33218		
30............	1.33192	1.33194	1.33190	

TABLE IV.

Absolute Index of Refraction of Water, Sodium Light.

Temp.	Kettler.	Hall-Payne.	*dn/dt.*	Temp.	Kettler.	Hall-Payne.	*dn/dt.*
15° C....	1.33365	1.33377	−0.00008	60° C..	1.32753	1.32754	− .00019
20......	1.33327	1.33335	− .00009	65.....	1.32655	1.32652	− .00020
25......	1.33281	1.33287	− .00011	70.....	1.32551	1.32547	−0.00021
30......	1.33226	1.33228	− .00013	75.....	1.32442	1.32434	−0.00022
35......	1.33164	1.33157	− .00014	80.....	1.32330	1.32323	−0.00023
40......	1.33093	1.33087	− .00015	85.....	1.32215	1.32208	−0.00024
45......	1.33017	1.33011	− .00016	90.....	1.32096	1.32086	−0.00025
50......	1.32934	1.32930	− .00017	95.....	1.31971	1.31959	−0.00026
55	1.32847	1.32846	− .00018	100.....	1.31843	1.31819	−0.00030

Kettler made observations for sodium light at nine different temperatures ranging from 20.9° to 95.17° C. inclusive. From these nine observations by extrapolation and interpolation he gives a table of values from − 10° to 200° C., from which table the values given above are taken. We now know that extrapolation from the range he used to the zero point is not justifiable owing to the rapidly decreasing numerical value of dn/dt as the freezing point is approached. Extrapolation is also not justifiable near the boiling point because of the rapidly increasing numerical value of dn/dt. This rapid increase in the numerical value of dn/dt as the boiling point is approached is probably due to the increasing quantities of water vapor in the water.

Empirical Formulas.—Numerous empirical formulas have been proposed connecting the index of refraction of water with the temperature. Dufet[1] proposes

$$n = n_0 - 10^{-7}(125.5t + 20.642t^2 - 0.00435t^3 - 0.00115t^4),$$

where n represents the refractive index at the temperature t° C., and n_0 the refractive index at 0° C. This formula was arrived at by setting up an empirical equation for dn/dt, from the best data available at that time in the range below 50°, and integrating. As tested by the writers the equation is not applicable to temperatures above 50° C. Walter's formula,

$$n = n_0 - 10^{-6}(12t + 2.05t^2 - 0.005t^3),$$

a modification of Dufet's formula, holds well over the range studied by Walter, that is, from 0° to 30° C. It does not hold for higher ranges. Owing to the relatively low values of dn/dt near the freezing point and the relatively high values near the boiling point a single simple equation covering the entire range from 0° to 100° cannot be expected to have a high accuracy over the entire range. The writers propose

$$n = 1.33401 - 10^{-7}(66t + 26.2t^2 - 0.1817t^3 + 0.000755t^4).$$

Walter's value for n_0, viz., 1.33401, is used. This equation was obtained by substituting in the general form, $n_0 - n = at + bt^2 + ct^3 + dt^4$, the values of n and t for four different temperatures and solving the four simultaneous equations for a, b, c, and d. This was done for four sets of equations, using different temperatures in the different sets and taking a mean of the values thus obtained. Some slight adjustments were then made by inspection and trial. The equation was tested at every five-degree point between 0° and 100°, and the maximum error was found to be at 75° where the deviation from the observed value is + 7 units in the fifth decimal place.

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[1] Jour. de Physique, 4, 389, 1885.

Osborn (loc. cit.) has given an empirical relation for the value of *dn/dt* which agrees very closely with experiment for the range 0° to 40° C. It is, however, not applicable above 50° C.

A number of empirical relations connecting the refractive index of a liquid with the density of the liquid have been proposed. Of these only two will be mentioned. Gladstone and Dale[1] have proposed the relation $(n - 1)/d = R$, where n is the index of refraction, d the density, and R a constant. Lorenz[2] proposed

$$\frac{n^2 - 1}{n^2 + 1} \cdot \frac{1}{d} = P, \text{ a constant.}$$

Table V. gives the values of R and P for water, the densities being taken from the sixth edition of the Smithsonian Tables.

TABLE V.

t.	*R.*	*P.*	*t.*	*R.*	*P.*	*t.*	*R.*	*P.*
15°...	0.33370	0.28030	50°..	0.33291	0.28030	90°.	0.33201	0.28079
20....	.33357	.28026	60...	.33276	.28043	95..	.33187	.28087
30....	.33336	.28023	70...	.33249	.28051	100..	.33163	.28088
40....	.33309	.28019	80...	.33221	.28063			

Getman and Wilson[3] give a few values between 15° and 40° C. for the refractive index and for R for water. Their values for the range studied are higher for the refractive index and R, and lower for *dn/dt* than those obtained by other observers, including the writers.

Ethyl Alcohol and Carbon Bisulphide.—A large number of determinations of the index of refraction of ethyl alcohol and carbon bisulphide have been made, but so far as the writers are aware no determinations have been made in the temperature ranges approaching the boiling points of either liquid. In connection with these liquids the second form of prism only, with automatic temperature control, was used. The same general procedure was followed and the same degree of accuracy reached as in the case of water. Here, however, the materials were not specially purified. Kahlbaum's ethyl alcohol, 99.8 per cent. absolute, and J. T. Baker and Co.'s carbon bisulphide were used. The analysis furnished by the makers for the carbon bisulphide was sp. gr. 1.27, N.V.M. 0.001 per cent., SO_2, H_2S, SO_3 none.

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[1] Phil. Trans., 1858, p. 887.

[2] Wied. Ann., 11, 77, 1880.

[3] Amer. Chem. Jr., 40, 468, 1908.

Determinations were made of the index of refraction of ethyl alcohol for fifty different temperatures between the limits of 15° and 75° C. These represent a number of runs each taken throughout the temperature range, the observations extending over several months. The values obtained were plotted on a large scale from which plot the results given in Table VI. were taken.

TABLE VI.

Index of Refraction, Relative to Air, of Kahlbaum's Ethyl Alcohol, 99.8 Per Cent. Absolute, for Sodium Light.

t.	*n.*	*t.*	*n.*	*t.*	*n.*	*t.*	*n.*
14° C....	1.36290	30° C...	1.35639	46° C...	1.34969	62° C...	1.34279
16......	1 36210	32......	1.35557	48......	1.34885	64......	1.34189
18......	1.36129	34......	1.35474	50......	1.34800	66......	1.34096
20......	1.36048	36......	1.35390	52......	1.34715	68......	1.34004
22......	1.35967	38......	1.35306	54......	1.34629	70......	1.33912
24......	1.35885	40......	1.35222	56......	1.34543	72......	1.33820
26......	1.35803	42......	1.35138	58......	1.34456	74......	1.33728
28......	1.35721	44......	1.35054	60......	1.34368	76......	1.33626

Determinations were made of the index of refraction of carbon bisulphide at forty-three different temperatures between the limits of 15.95° and 44.7° C. These determinations represent many runs taken throughout the temperature range. These results were plotted and Table VII. made.

TABLE VII.

The Index of Refraction of Carbon Bisulphide, Relative to Air, for Sodium Light.

t.	*n.*	*t.*	*n.*	*t.*	*n.*	*t.*	*n.*
15° C....	1.62935	24° C...	1.62226	34° C...	1.61413	44° C...	1.60582
16......	1.62858	26......	1.62064	36......	1.61247	45......	1.60499
18......	1.62704	28......	1.61902	38......	1.61080		
20......	1.62546	30......	1.61740	40......	1.60914		
22......	1.62387	32......	1.61577	42......	1.60748		

TABLE VIII.

Values of dn/dt for Ethyl Alcohol and Carbon Bisulphide.

Temperature.	Ethyl Alcohol.	Carbon Bisulphide.
15° C....................	−0.00040	−0.00077
25......................	− .00041	− .00081
35......................	− .00042	− .00082
45......................	− .00042	− .00083
55......................	− .00043	
65......................	− .00045	
75......................	− .00046	

If n represents the index of refraction at any temperature $t°$ C., and n' the index of refraction at 15° C., then as an empirical equation we may write

$$n = n' - 10^{-6}[a(t - 15) + b(t - 15)^2 + c(t - 15)^3].$$

For ethyl alcohol for the range 15° to 70° $n' = 1.36250$, $a = 404$, $b = 0.22$, $c = 0.0025$.

For carbon bisulphide for the range 15° to 45° $n' = 1.62935$, $a = 766$, $b = 2.56$, $c = -0.035$.

Andrews[1] has made determinations on the index of refraction of ethyl alcohol, giving great care to the purity of the alcohol. His value, which he believes correct to one unit in the fifth place, at 25° C., for sodium light is 1.359408. The writers' value at this temperature is 1.35844. The writers believe this difference in observed value of the index is due to the difference in purity. For carbon bisulphide at 20° C. and for sodium light Landolt-Bornstein Tabellen give 1.62772 as the mean of the values obtained by four observers. The writers' value is 1.62546. Again the only explanation that can be offered is the difference in purity of the material. While slight impurities will change the value of the index of refraction, it is hardly to be expected that they would produce a large change in the value of dn/dt and it is the change in the refractive index with the temperature, rather than the value of the index for pure material that is emphasized in the case of alcohol and carbon bisulphide.

UNIVERSITY OF CALIFORNIA,
DEPARTMENT OF PHYSICS.

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[1] Amer. Chem. Soc. Jr., 30, 353, 1908.

MEASUREMENT OF MERCURY VAPOR PRESSURE BY MEANS OF THE KNUDSEN PRESSURE GAUGE.

By Charles F. Hill.

Synopsis.

Vapor Pressure of Mercury, 0 to 35° C.—The disagreement among the results obtained by previous observers for this range of temperature suggested the need for a *direct determination* of the vapor pressures *with a Knudsen gauge.* Impurities were eliminated by numerous distillations in a system cut off from the pump by a liquid air trap, and the slight amount of residual gas was corrected for. The readings obtained at 19 temperatures lie near a smooth curve which, it is believed, gives the vapor pressures to within 3 per cent. The values for 0, 10, 20, and 30° C. are, respectively, .000350, .000775, .00182 and .00407 mm. of Hg, considerably higher than those obtained by Knudsen in 1909, but agreeing fairly well with Morley's results up to 15°, and at higher temperatures with values extrapolated from the results of Ramsey and Young.

Historical.

While engaged in experimental work in the spring of 1920, an accurate knowledge of the vapor pressure of mercury at room temperature became of importance. On looking for the values given in tables for temperatures below 40° C. very little agreement among the various observers was found as may be seen in the following table.

Table I.

T.	Regnault 1862.	Hagen 1882.	Hertz 1882.	Ramsey and Young 1886.	Van der Plaats 1886.	Morley 1904.	Knudsen 1909.
0°	.02	.015	.00019	——	.00047	.0004	.000184
10°	.0268	.018	.0005	——	.0008	.0008	.0005
20°	.0372	.021	.0013	——	.0013	.0015	.00188
30°	.053	.026	.0029	——	——	.003	.00278
40°	.0767	.033	.0063	.008	——	.006	.006
50°	.112	.042	.013	.015	——	.011	.0126
60°	——	——	——	——	——	.021	——
70°	——	——	——	——	——	.04	——

In 1886 van der Plaats[1] published results obtained by taking a large number of readings between 0 and 20° Centigrade. Values from his mean curve are usually given preference in tables. The method was to pass dry gas through water, through sulphuric acid, and then through mercury until saturated, after which the mercury was collected by gold and pumice stone and weighed. The vapor pressure was calculated from the data obtained by comparison with the vapor pressure of water.

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[1] Rec. Trans. Chim., 5, p. 49, 1886.

Van der Plaats' readings show considerable variation, but are consistent enough so that with the number of readings taken his results must be given considerable weight. The method would not be expected to give values too high since his chief error should be loss of evaporated mercury.

E. W. Morley[1] in 1904 used practically the same method as van der Plaats except that the evaporated mercury was measured by weighing the sample before and after evaporation. Readings were taken at 16, 30, 40, 50, 60 and 70° C., and Dalton's equation

$$P = ab^t$$

was used for the calculation of the mean curve and for extrapolation to 0° C. Morley's readings at 40, 30 and 16° C., are from 8 to 20 per cent. below his mean curve but at the higher temperatures his values agree with those given by others. Vapor-pressure curves should have a decreasing per cent. increase as the temperature increases. Morley's curve is perfectly uniform if the slope is measured in this way, but the error in the readings at low temperatures could easily account for this fact. While Morley can not claim a high percentage accuracy his agreement with van der Plaats at low temperatures, and with the other observers at higher temperatures, seems to indicate that the order of his values is correct.

The last data of importance published were those of Knudsen[2] in 1909. An equation was developed for the flow of gas through a tube with a small opening over one end, and an apparatus based on this equation was arranged so that the vapor pressure of mercury could be measured. This equation

$$G = \sqrt{\frac{p' - p''}{W' + W''}} \times t$$

involves the pressure difference, the resistance of tube and opening, the density of the gas and the time. G is the mass of the gas or vapor which will flow through the small opening in an evacuated tube, as shown in Fig. 1, with a pressure difference $p' - p''$. In practice p'' was made zero by the application of a cold bath to B. Knudsen's results obtained by this method are about one half as large as those of Morley, and also of van der Plaats, in the region 0 to 40° C. The fact that mercury requires an appreciable time for evaporation might tend to produce such an effect since p' at the opening is being relieved continuously.

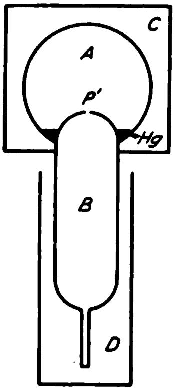

Fig. 1.

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[1] Phil. Mag., Vol. –, p. 662, 1904.

[2] Ann. der Physik. 28, p. 75, 1908–9; ibid., 28, p. 999, 1908–9; ibid., 29, p. 179, 1909.

Experimental.

From the foregoing it seems desirable that there should be additional experimental data taken at ordinary working temperatures. The Knudsen pressure gauge, in the opinion of the writer, offered the most dependable method for such measurements since in its action it is independent of the nature of the gas, and also its range is approximately that of the vapor pressures to be measured. The Knudsen gauge available was not arranged to be used as an absolute manometer, but was calibrated by means of an accurately constructed McLeod gauge. The principle upon which the Knudsen[1] gauge depends is that the molecules of a residual gas in a partial vacuum are thrown off from a heated platinum foil, and striking a light and suitably suspended vane exert a couple, thus producing a deflection which may be read by means of an optical system. The deflection for zero pressure of course is zero. This fact makes it possible to use a McLeod gauge for calibration purposes, since calibration curves may be used with the origin as an accurately determined point. The McLeod gauge may be read quite accurately to .001 mm., or even less, provided the glass and mercury are kept clean.

A special pyrex glass McLeod gauge was constructed for the purpose and fused directly to the rest of the apparatus (including the Knudsen gauge) which was also of pyrex glass. The volume tube of the McLeod gauge was made comparatively large in order to lessen friction and surface-tension effects. The gauge was found to read consistently to .0005 mm. if the mercury and glass were kept clean. The apparatus was assembled as shown in Fig. 2. The Knudsen gauge A, and the sample container B, were rigidly supported within a tight asbestos lined wooden box. The apparatus within the box was connected to the pumping

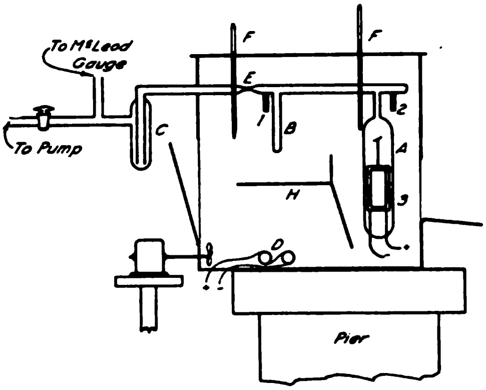

Fig. 2.

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[1] Ann. der Physik, 32, pp. 809–842, 1910; Phys. Rev., 12, pp. 70–80, 1918.

system and McLeod gauge without through a tube of rather large diameter and including a mercury trap *C*. The system was evacuated by means of a Langmuir condensation pump supported by a Gaede rotary mercury pump. By continued pumping and with liquid air surrounding the trap *C* the pressure was readily brought down to about .005 mm. Hg. It was then further reduced by approximately equal steps. At each step the pressure as indicated by the McLeod gauge was accurately read simultaneously with the deflection of the Knudsen gauge, while a given constant current flowed through the platinum foil of the gauge. In this way data for a calibration curve were obtained. To test the consistency of the readings (for both gauges) sets of data were taken in which the current supplied to the gauge had in turn the values .3, .4, .5, .6 ampere. This data when plotted on 40 cm. coördinate paper gave, for each set, a smooth curve, showing that the two gauges were at least consistent.

The sample of mercury was then introduced into the container *B* and with liquid air surrounding the trap *C*, and the pumps running, the mercury was distilled slowly out of the container *B* and back again by heating first the container and then the rest of the tube. This process of distillation was carried out a number of times. Warm water was kept on the sample to prevent loss of the sample and condensation of vapors while the entire tube within the asbestos-lined box was heated to a temperature of 250 to 300° C. for several hours in order to drive the vapors out of the walls of the tube. The apparatus was then sealed off at *E*. After allowing the box to come to the desired temperature for a time, the total pressure was taken. The mercury was then driven into the container *B*, while submerged in liquid air, by warming the rest of the tube, and the residual gas pressure measured. The difference between the total and the residual pressures is the vapor pressure of the mercury. Readings were thus taken at a number of temperatures over the range 0 to 35°. After completing the series the tube was opened, resealed to the pump and the same process of distillation and heating carried out again. This method was continued until minimum values for the vapor pressure were obtained on three successive sets of readings. The mercury was considered pure at this point.

Another calibration of the Knudsen gauge was now carried out, a second sample of mercury, purified with nitric acid, was introduced and the process of distillation and heating was repeated eight times. The tube was then sealed off again at *E* and readings were taken at several different temperatures.

The four sets of data obtained in this way contained nineteen individual values for the vapor pressure of mercury extending over the temperature interval of −.7 to 34.9° Centigrade. Of these values two or three differ from the mean curve by about 6 per cent., the rest being within 3 per cent. of the curve. In the following discussion it will be shown that this is about the accuracy that could be expected from the method.

The temperatures within the asbestos-lined box were read by means of two tenth-degree mercurial thermometers placed at different points. To insure uniform temperature the air was caused to circulate within the box by a fan driven by a motor without. The fan system was supported separately from the pier and box to prevent jarring the Knudsen gauge. The circulation of the air was directed by the bafflers *H*. Two heating coils, *D*, controlled the high temperatures, while the low temperatures were obtained by opening the windows and cooling the room. In general the temperatures were held constant, probably at .1 or very readily at .2° C. Changes of .2° in the box temperature produced changes in the vapor pressure that were just detectable by the Knudsen gauge. The gauge did not register changes as quickly as the thermometers. The Knudsen gauge was read by a lamp and scale at one meter distance. In order to hold the zero point, or rather to hold the vane and foil at a constant distance, the scale was rigidly fixed to the floor. If the vane became displaced, it could be brought back to its original position by merely restoring the zero on the scale. One set of calibration curves was used for three sets of data, and between each set the calibration was checked to make sure that it remained constant.

In order to determine the probable accuracy of the method some of the sources of error and their probable magnitude will now be considered. In the first place, impurities tend to increase the vapor pressure in the tube, so that this method would be expected to give values too high. The first sample gave minimum values for about eight distillations, and since the process of distillation was carried out more than twenty times, this error was considered eliminated. The second sample was first treated with nitric acid and then distilled eight times, hence we were justified in considering that the errors due to impurities in this sample were negligible. Special care was taken to keep the McLeod gauge and the mercury in it clean in order to prevent changes in friction. It was found that upon taking several readings at the same pressure the gauge could be read to within a total range of ± 2 per cent., except at the low pressures and these seemed to check well with the other readings as shown by the curves. The accurately known point on the curve at the origin helped to take care of this source of error. There was a variation of 3 per cent. in the Knudsen gauge readings, however, if a new set of calibration curves were drawn through the same points, a variation would be obtained that would account for most of this error. Allowing for a probable error of ± 2 per cent. for temperature variations and the same for each of the other sources of error, the total probable error should be within about ± 6 per cent. The fact that this is the range of the actual readings seems to indicate that the principle sources of error have been accounted for and the data are about what one should expect from the method.

TABLE II.

Third Run of Data.

I.	R_0.	R.	Deflection.	Total Pressure from Curve.	Mean.	Temperature.
.3	9.8	13.0	3.2	.00277		
.4		15.3	5.5	.00274		25°
.5		18.0	8.2	.00276		
.6		20.9	11.1	.00272	.00275	
.3	10.0	14.32	4.32	.00432		
.4		17.3	7.3	.00438		30.8
.5		20.7	10.7	.00422		
.6		24.5	14.5	.00416	.00427	
.3	10.0	15.0	5.0	.0055		
.4		18.55	8.55	.00556		34.3
.5		22.5	12.5	.0054		
.6		26.75	16.75	.00514	.00540	
.3	9.7	11.05	1.35	.00087		
.4		12.02	2.32	.00088		
.5		13.19	3.49	.00089		11.6
.6		14.5	4.8	.00088	.00088	
.3	10.2	10.8	.6	.00033		
.4		11.17	.97	.00036		–.7
.5		11.7	1.5	.00036		
.6		12.35	2.15	.00036	.00035	
				Residual Pressure from Curve.		
.3	10.15		deflection hardly	perceptible		
.4		10.19	.04	.00002		
.5		10.23	.08	.00002		
.6		10.28	.13	.00002	.00002	

One set of the actual readings taken is given in Table II. which constituted the third run in the first series. The total pressure for a given temperature is given in the fifth column for different values of current flowing through the Knudsen gauge. The mean of these is recorded in the sixth column. At the bottom of the table is the data giving the residual gas pressure. Obviously the total pressure less this gas pressure is the vapor pressure of mercury. Table II. contains the data for the vapor pressure of mercury at five different temperatures. A second series, in which a new sample of mercury cleaned with nitric acid as noted earlier, gave values of the vapor pressure for additional temperatures. Together the two series gave nineteen values extending over a range in temperature from − .7 to 34.9° C. which are collected in Table III. The corresponding graph is shown in Fig. 3. The points all lie well upon a smooth curve. In Table IV. the vapor pressure of mercury in mm. is given for 2-degree intervals taken from the curve.

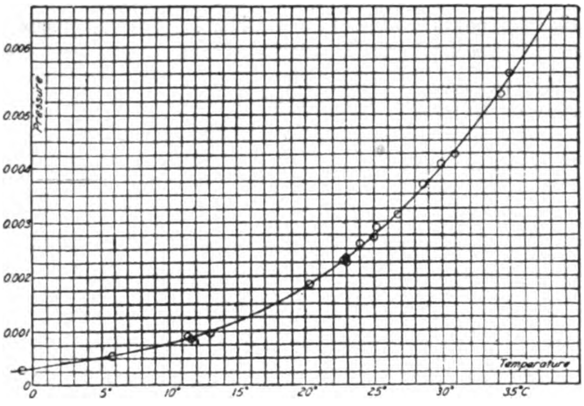

Fig. 3.

TABLE III.

Values for the Vapor Pressure of Mercury at Various Temperatures.

Temperature.	Pressure mm. Mercury.	Temperature.	Pressure mm. Mercury.
-.7°	.00033	24.0°	.00262
5.7	.00055	25.0	.00273
11.4	.00092	25.6	.00292
11.6	.00086	26.8	.003145
11.6	.000815	28.6	.0037
13.0	.00097	29.9	.004075
20.3	.00187	30.8	.00425
22.8	.00230	34.3	.00538
23.0	.00224	34.9	.00575
23.0	.00235		

In conclusion, the author wishes to thank Professor A. P. Carman for the use of the facilities of the laboratory, and also to thank Professor

C. T. Knipp for the interest he has taken in the work and for the many suggestions offered.

TABLE IV.

Values for Each 2° as Taken from Smooth Curve Through the Points.

0.0°	.000350 mm. Hg.
2.0	.000412
4.0	.000487
6.0	.000572
8.0	.000662
10.0	.000775
12.0	.000895
14.0	.00105
16.0	.00126
18.0	.00150
20.0	.00182
22.0°	.00214 mm. Hg.
24.0	.00234
26.0	.003
28.0	.0035
30.0	.00407
32.0	.00467
34.0	.00535
36.0	.00607
38.0	.00695
40.0	.008

LABORATORY OF PHYSICS,
UNIVERSITY OF ILLINOIS.

ON THE AGEING EFFECT IN THE MOBILITY OF POSITIVE GAS IONS.

By H. B. Wahlin.

Synopsis.

Mobility of positive ions of air immediately after formation has been found by Erikson, using a modified Zeleny method, to be much higher than the normal value. This result has been verified by the author using the alternating potential method. Ions formed in an ante-chamber by α-rays from polonium were driven by a weak auxiliary field into the measuring chamber where the mobility was determined by the use of an alternating field of 1,800 to 3,600 cycles and of variable strength. Pure dry air was used at a pressure of 30 mm. When the auxiliary potential was 1.5 volts the measured mobility was normal but when the potential was 3.0 volts or more the mobility rose to 1.80 cm./sec./volt/cm., indicating that the ions entered the measuring chamber before they were aged. The time required for the ions to age or reach the normal condition is estimated to be between 1/75 and 1/120 of a second.

At the November meeting of the American Physical Society, Professor H. A. Erikson, of the University of Minnesota, presented a paper on the variation in the mobility of positively charged gas ions with time. Using a modification of the Zeleny method for measuring mobilities Professor Erikson[1] has shown that if the determinations are made immediately after the ions are formed, the values obtained are for air, oxygen, and nitrogen much higher than the accepted values. If, however, the ions are aged for an appreciable time Erikson found this time to be of the order of 1/100 of a second (for air) before the determinations are made, the mobility falls to the normal value (1.37 cm. per sec. per volt per cm.).

In order to investigate this effect further, the writer constructed an apparatus on the principle of the Franck modification of the Rutherford alternating potential method for determining mobilities using α-particles from polonium as the ionizing source. As a source of alternating potential, an oscillating vacuum-tube circuit of the Hartley type (Fig. 1) with a telephone transformer (T) in the plate circuit was used. The voltage on the secondary of the transformer was varied by varying the potential of the plate by means of the potential dividing resistance R_2. In order to keep the frequency of the alternating potential constant with a variation in the plate voltage, a resistance (R_1) was introduced into the grid circuit of such a value that the potential could be varied over the desired range without any noticeable effect on the frequency.

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[1] Erikson, Phys. Rev., 17, p. 400; 18, p. 100.

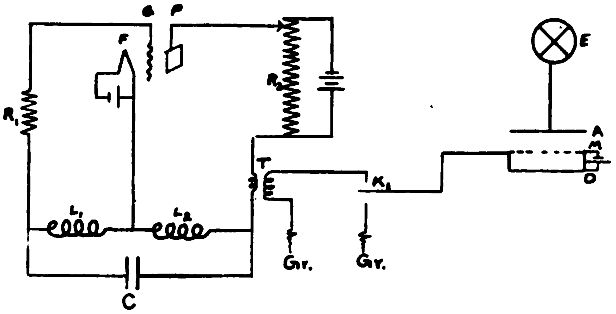

Fig. 1.

The inductances (L_1, L_2) and the capacity (C) were chosen so as to give a range of frequencies from 1,800 alternations per second to 3,600 alternations per second. One terminal of the secondary of the transformer was grounded, and the other was connected through a condenser key (K_1) to the gauze (M). On the lower side of this gauze a copper plate coated with polonium was fastened in such a manner that the radiation from the same was confined to the lower half of the region between M and D. The gauze was made by boring holes 1.3 mm. in diameter in a brass plate .5 mm. thick. The distance between centers of adjacent holes was 4 mm. The diameter of the gauze was 10 cm. This gauze was fastened to a fiber ring which rested on the brass plate (D). The distance between M and D was 1 cm. Between the gauze and the brass plate a source of potential was fastened for driving the ions through the gauze into the measuring field. A represents a collecting plate 10 cm. in diameter. The distance between A and M was varied between the limits of 6 mm. and 9 mm. The collecting plate in turn was connected through a platinum wire "bow switch" to the electrometer (E). The electrometer was of the Compton type with a gold sputtered quartz fiber as a suspension and was used at a sensibility of 4,500 scale divisions per volt with the scale at a distance of 150 cm. The amount of charge given to A in a given time was taken as a measure of the current. Then from the value of the alternating potential at which the ions cease to get across to the collecting plate the mobility may be calculated from the expression

$$K = \frac{\pi n d^2}{\sqrt{2}\, V} \frac{P}{760}, \tag{1}$$

where K is the mobility at a pressure of 760 mm., P is the pressure, n the frequency, and V is the alternating potential.

In all these determinations air was used at pressures ranging from 1 cm. to 3 cm. of mercury. A number of mobility curves were obtained at each pressure with values of the auxiliary field between *M* and *D* varying in some cases between 1.5 volts and 60 volts.

The air was purified by passing it over hot copper oxide to break up organic impurities. This would also remove the hydrogen. It next passed over potassium hydroxide to remove carbon dioxide and then through calcium chloride and phosphorous pentoxide to remove water vapor, and finally into the chamber containing the plates *A*, *M* and *D*. Before taking a series of readings, the chamber was washed out by exhausting to a pressure of 1 mm. or less and filling to atmospheric pressure. This was repeated three or four times, so that the residual gas left in the chamber from the previous filling was very small. In order to prevent any contamination of the gas by vapors from the walls of the chamber, the readings were taken immediately after making a filling. However, there was no noticeable difference produced in the results by allowing the gas to remain in the chamber for some time.

If the effect observed by Erikson is correct, we should expect that for low values of the auxiliary field between *M* and *D*, the ions would remain in this field long enough so that by the time they are carried through the gauze they will be aged, and that the intercept of the mobility curve on the voltage axis would give the normal value of the mobility. However, as the auxiliary field is increased ions would get through the gauze before ageing and the intercept would give values for the mobility which are abnormally high. As will be seen from Fig. 2, this is the case, for

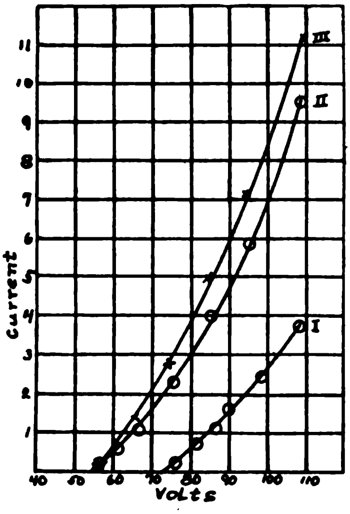

Fig. 2.

Frequency of alternating potential, 1,800 alternations per second. Plate distance *d*, 8 mm. Pressure of gas, 30 mm. Curve I., Auxiliary field, 1.5 volts. Curve II., Auxiliary field, 3.0 volts. Curve III., Auxiliary field, 4.5 volts.

with an auxiliary field of 1.5 volts the value for the mobility is 1.35 cm. per sec. per volt per cm., and with an auxiliary field of 3.0 volts the value rises to 1.80 cm. per sec. per volt per cm. A further increase in the auxiliary field does not change the intercept, as may be seen from the fact that the intercept for a field of 4.5 volts is the same as for 3.0 volts. The slight tendency shown by curve number 1 to be concaved upwards is probably due to the fact that the gauze and the collecting plate were not accurately parallel, for since the distance between these two is of the order of 8 mm. and since in the expression for the mobility constant (equation 1) this distance enters as the square, a small variation in this distance would produce quite an appreciable effect in altering the shape of the curve. The increased concavity of curves 2 and 3 is probably due to the fact that theions passing through the gauze are both the aged and unaged variety. The estimated time necessary for ageing is for all the curves taken somewhere between 1/75 and 1/120 of a second.

DISCUSSION OF RESULTS.

Erikson has been unable to notice any ageing in the mobility of the negative ion. In this case, however, the effect is complicated by the fact that we have a distribution of mobilities between electronic and ionic. Determinations of the mobilities of the negative ions have shown that in most gases the mobility constant becomes abnormally high as the pressure is decreased. This would indicate that the electron does not attach itself immediately to a molecule but will travel some distance through a gas before uniting to form a negative ion. It would seem from this then that a further change after the electron once has attached itself is not very probable.

The most obvious explanation of the results given above is on the basis of a cluster theory of ion formation. On such a theory the formation of a positively charged gas ion would consist first in the detachment of an electron from the neutral molecule to form the positive ion and then the attachment of molecules to this ion to form the cluster. Then if the mobility is measured before this clustering takes place, the mean free path of the ion would be greater and as a consequence the mobility higher.

If, however, a cluster is formed, it is to be expected that it will disintegrate if the field in which the mobility is measured becomes high enough and the mobility will rise to a value limited principally by the size of the molecule or atom which forms the nucleus of the cluster. This question has been investigated by Loeb,[1] Chattock, Tyndall, and others without obtaining any evidence for an increase in the mobility.

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[1] Loeb, PHYS. REV., December, 1916.

Wellisch, Franck, Franck and Meitner, and Rutherford have found that for a given gaseous medium the mobility is independent of the nature of the carrier as long as it is of atomic dimensions. On the basis of a small ion theory it is therefore to be expected that an aged ion would have the same mobility as an unaged one. However, these results can be coördinated on the basis of a cluster theory if the ions used by these observers were aged before the mobility was determined and if the size of the cluster is independent of the carrier which forms the nucleus.

In conclusion, the writer wishes to express his thanks to Mr. J. P. Foerst for his work in connection with the construction of the apparatus used in these determinations.

University of Wisconsin,
Madison, Wisconsin.

THE EFFECT OF DISSOLVED SUBSTANCES ON THE DEPOSITION OF COLLOIDAL PARTICLES FROM A SOLUTION BY MEANS OF AN ELECTRIC CURRENT.

BY RICHARD D. KLEEMAN.

SYNOPSIS.

Effect of Various Dissolved Substances on Porcelain Slip (a Colloidal Solution of Particles of Clay, Flint, and Feldspar in Water).—(1) *Effect on compactness of deposit produced by an electric current.* It was found that the addition of only from 0.1 to 0.3 per cent. of any one of a number of substances, including Na_2SiO_3, Na_2SO_4, Na_3PO_4, Na_2HPO_4, H tartrate, Na tartrate, NaOH and KOH, resulted in a deposit which, though not quite dry, was solid instead of being semi-liquid. The compactness does not depend on the current density. As the amount of substance added is increased, the compactness increases less and less and soon reaches a limiting value. The full effect of the substance does not appear at once but only after a period which varies up to several hours. (2) *Effect on the fluidity of the slip* is to increase it markedly. From the relative action of different substances this effect is intimately related to the first one. Although the result of adding the substance is first to precipitate some of the particles, when more solid material is added the precipitate is redissolved so that for the same fluidity the proportion of solid dissolved is much greater with the added substance than without. (3) *Suggested explanation.* Both effects may be explained if we assume that the radii of the spheres of action of the particles of the slip are diminished by the dissolved substance. Particles will go into colloidal solution if no combinations result from encounters. This property is expressed in terms of the interfacial surface tension of the particles. *The equations of distribution of colloidal particles under the action of gravity* are obtained and with their help an explanation of the effect mentioned above, the precipitation and re-solution of the particles of the slip, is suggested. From a consideration of the experimental results it is concluded that the volume of the *spheres of action of a particle in porcelain slip* is about double the actual volume of the particle.

DURING some experiments on the electric deposition of porcelain slip it was observed that the deposit obtained from the slip used in the wet porcelain process (in which the slip is cast into molds of plaster of Paris) was solid though not quite dry, while that obtained from slip used in the dry process was of the consistency of thick cream. It was soon found that the difference in the nature of the deposits obtained was due to the small quantity of sodium silicate (Na_2SiO_3) that is mixed with the slip used in the wet process. Porcelain slip, it should be mentioned, consists of a colloidal solution of particles of clay, flint, and feldspar, in water. A systematic investigation was next carried out with the assistance of Mr. Chase to determine the effect of various dissolved substances on the nature of the deposit obtained. It was found that besides sodium silicate the substances Na_2SO_4, Na_3PO_4,

Na_2HPO_4, H tartrate, Na tartrate, NaOH, KOH showed the effect very well, and in fact it was found that most substances showed the effect in a more or less degree.

The hardness or compactness of the deposit obtained increased with the amount of substance added. It was difficult, from the nature of things, to obtain definite quantitative results. It may, however, be remarked that in a general way the compactness of the deposit appeared to increase at first rapidly with the amount of substance added, and gradually less so till a point was reached beyond which further addition of the substance did not produce any appreciable effect, the relation between amount of substance added and compactness of deposit obtained thus resembles a saturation curve. The minimum amount of substance necessary to add in order to produce the maximum compactness was usually very small, it was difficult to determine exactly in any given case for reasons that follow from the preceding remarks. The order of the quantity is 1 part in 300–1,000 by weight. The full effect of the substance added does not appear at once, but after a time which may vary from a quarter of an hour to several hours. Stirring seems to help the final state being reached more rapidly.

The compactness of the deposit obtained with slip containing one of the substances mentioned did not seem to depend on the density of the current used, provided that it was not so large that the gases evolved interfered with the deposition. Very small current densities were occasionally used, of the order of a milliampere and less, so that it was necessary to let the current flow for hours to obtain a deposit a quarter of an inch thick, but the compactness of the solid deposit obtained did not seem to be different from that obtained with larger currents. Scarcely any transition layer seemed to exist between the deposit and the slip, whatever the current density, and a short exposure of the deposit to the air was therefore sufficient to dry its surface. This effect was specially noticeable when sodium silicate was added to the slip.

The increase in compactness of the deposit, obtained on the addition to the slip of one of the substances mentioned, was found to be intimately connected with the increase in fluidity of the slip which was found to be produced by these substances. The connection between the two effects may be well illustrated by the following typical experiment. Suppose that a deposit is obtained electrically from pure slip containing about 30 per cent. of solid matter by weight. The deposit will be of the consistency of thick cream. Now let a small quantity of Na_3PO_4, about one part in three hundred by weight, be added. This will give rise to a partial precipitation of the particles of the slip, the flint and feldspar particles mainly being affected. But this precipitate goes into solution again on adding additional solid matter. Now we may go on adding solid matter till a point is reached when the fluidity of the slip is the same as that it possessed before the addition of Na_3PO_4. It will then contain about 60 per cent. of solid matter by weight, or about double the amount it possessed initially. The amount of solid added may be taken as a measure of the increase in fluidity produced by the dissolved substance. The deposit obtained from the slip will now be in a solid instead of in a semi-liquid state. Similarly the connection between the two effects may be traced in the case of other substances, and for different amounts of a substance added. It was found that an increase in the compactness of the deposit, as far as such a thing could be judged, was attended by an increase in the fluidity of the slip as measured in the foregoing manner, or by the rate of its flow.

The relation between the two effects may be very simply and strikingly explained by assuming that the addition of a small amount of a substance to the slip decreases the radii of the spheres of action of the particles, or the spheres associated with the particles which do not penetrate into each other during their motion of translation. The particles would then pack more closely on being deposited by an electric current, and the fluidity of the solution would be increased since the particles would possess more freedom of motion with respect to each other.

We may obtain some information about the sphere of action of a particle from increase of fluidity considerations. The addition of a small quantity of Na_3PO_4 of one part in three hundred by weight to the slip, we have seen, necessitates doubling the amount of solid matter in order to keep the fluidity constant. It may be taken as a first approximation that the total volume of the spheres of action of the particles in the slip was not changed during the process. It would then follow that the volume of the sphere of action of a particle in the slip was decreased to half its value through the addition of the Na_3PO_4, and that the volume of the former sphere of action is, therefore, greater than twice the volume of the particle. This appears to be borne out by experiments on the amount of water content in the deposit from *pure slip* by an electric current, which was found to be about one half of the total volume of the deposit. Experiments with clay alone gave in this manner a value of about two thirds, or a ratio of 3 to 1 of the total volume of the spheres of action of the particles to their actual volume.

If a small quantity of Na_3PO_4, about one part in three hundred by weight, is added to porcelain slip containing about 30 per cent. of solid matter, some of the particles are immediately precipitated and then a gradual process of precipitation goes on. On adding more solid matter and agitating the solution the precipitated particles may be brought into solution again and kept suspended. The experiment first of all shows that the radii of the spheres of action of the particles were decreased to about the actual volume of the particles by the addition of the Na_3PO_4. This is supported by the fact that the deposit obtained by an electric current is solid. The experiment also shows that the ability of particles to keep in suspension in a solution may depend on their number. A theoretical investigation of this point is given further on.

It will be of interest to point out in this connection that particles of flint and feldspar do not by themselves go into colloidal solution in water, but clay particles do, and that therefore in porcelain slip the flint and feldspar particles are kept in suspension in the solution by the clay particles.

We may now proceed to consider some theoretical aspects of the foregoing experiments, and of colloidal solutions in general. The condition that particles mixed with a liquid may remain in colloidal solution is that two particles on colliding should separate again, or that apparent forces of repulsion should come into play when two particles approach each other. These forces, it will be shown, may be expressed in terms of the interfacial surface tension of the particles in contact with the solvent. The surface tension of a liquid in contact with a solid is the external work done in separating two pieces of the substance in close contact submerged in the liquid per unit area of the surface of contact. The surface work of a particle is accordingly equal to the area of its surface multiplied by its interfacial surface tension. Hence when two particles approach one another in a liquid this would be attended by a change in their total surface work. If this increases, the corresponding external work is done by the particles at the expense of their kinetic energy, the effect being as if forces of repulsion were called into play on approach of the particles. Therefore if ΔW_s denote the increase in the surface work of two particles approaching one another, they will separate again if

$$\Delta W_s \geqq E,$$

where E denotes the kinetic energy of the particles. If the surface work W_s, or the interfacial surface tension is negative, which corresponds to external work being done by the system on producing additional interfacial surface, ΔW_s corresponds to a numerical decrease in W_s, while if ΔW_s is positive, or the surface tension is positive, W_s corresponds to a numerical increase in W_s. Therefore if the interfacial surface tension of the particles is positive, and two particles do not combine on collision, it follows that the formation of new interfacial surface would in the initial part of the process require the expenditure of external work, or apparent forces of attraction would come into play, while during the remaining part of the process the system would do work, or apparent forces of repulsion would come into play. These forces of repulsion prevent the particles from uniting, but it is evident that if by any chance the particles came into contact under the foregoing conditions, they would remain in contact. If however the interfacial surface tension is negative, the particles would separate again if brought into actual contact.

The area of the change in the transition surface for a given distance of approach of two equal colloidal particles would evidently on the average be proportional to the cube root of the mass of one of the particles, and the force of repulsion would increase in proportion. Hence if the kinetic energy of each particle were proportional to the absolute temperature, as is the case with a molecule in the gaseous state, and thus independent of its mass, the distance of approach of the particles would be the less the greater their masses. Hence under these conditions the chance of two particles combining would be the smaller the greater their masses. But the kinetic energy of a colloidal particle is not likely to be proportional to the temperature, nor at any temperature equal to that of a molecule in the gaseous state, as has been pointed out by the writer.[1] At present it is impossible therefore to say how the chance of combination of two particles depends on their size.

The boundary between a solid and liquid in contact we would expect to be the seat of a liquid transition layer. The density of the liquid in the layer would accordingly undergo a gradual change from one side to the other, and this may be attended by a separation of electrical charges. The work done in the production of the electrical layers, it should be noted, is *included* in the *interfacial surface tension*. In a separate paper under the title "A Transition or Adsorption Layer Theory of the E.M.F. of a Voltaic Cell," the nature and properties of this transition layer are discussed. The forces called into play on encounter of two colloidal particles are obviously in part directly due to the separated electrical charges of opposite sign associated with their transition layers. Thus the outside electrical layers of two particles of the same kind have the same sign, and forces of repulsion will therefore initially come into play on approach of the particles.

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[1] A Kinetic Theory of Gases and Liquids, by R. D. Kleeman, pp. 210–217. John Wiley & Sons, New York.

The distribution of the particles in a solution under the action of gravity is of importance to consider in this connection. The differential equation of equilibrium is

$$F \cdot \delta h = \delta P_s,$$

where P_s denotes the osmotic pressure of the particles at a distance h from the surface of the solution, and F the force due to gravity acting on the particles in a cubic cm. of the solution. If v_a denotes the volume of a particle, ρ_a its density, ρ the density of the liquid, we have

$$F = gv_a(\rho_a - \rho)N_c,$$

where N_c denotes the concentration of the particles. If the solution is dilute, the osmotic pressure of the particles obeys the gas laws, or

$$P_s = \frac{RT}{N} N_c,$$

where N denotes the number of molecules in a gram molecule. The equation of equilibrium may accordingly be written

$$mgN_c \cdot \delta h = \frac{RT}{N} \cdot \delta N_c, \tag{1}$$

substituting m for $v_a(\rho_a - \rho)$ the apparent mass of a particle. On integrating this equation we obtain

$$mgh = \frac{RT}{N} \log \frac{N_c''}{N_c'}, \tag{2}$$

where N_c' denotes the concentration of the particles in the surface of the solution, and N_c'' that at a distance h from the surface.

The foregoing concentrations may conveniently be expressed in terms of N_h the total number of particles in a cylinder of unit cross-section and height h. We have directly

$$\int_0^h N_c \cdot \delta h = N_h,$$

an equation which on being transformed by the help of equation (1) and integrated gives

$$N_c'' - N_c' = N_h \frac{Ngm}{RT}. \tag{3}$$

From this equation and equation (2) we obtain

$$N_c'(e^{\frac{Nmgh}{RT}} - 1) = \frac{N_h Ngm}{RT} \tag{4}$$

and

$$N_c''(e^{\frac{Nmgh}{RT}} - 1) = \frac{N_h Ngm}{RT} e^{\frac{Nmgh}{RT}}. \tag{5}$$

It appears from equation (2) that the ratio of the concentration of the particles corresponding to the upper surface and bottom of a solution is independent of the total number of particles provided their masses are kept the same. Therefore if a sufficiently large number of colloidal particles are added to a solution, the concentration of the particles at the bottom of the solution as given by equation (2) may be greater than that corresponding to the particles being in contact with each other. A layer of precipitated particles will accordingly form at the bottom of the vessel. But these particles will not differ from those in solution, and will readily go into solution again on adding a sufficient amount of liquid. The particles in the (apparent) precipitate would however not pack so closely as would be the case if they were dry, but their centers of mass would be separated by distances approximately equal to the diameter of their spheres of action when in solution. These considerations indicate another method for obtaining values of the radii of the spheres of action of colloidal particles in a solution.

We have seen that particles which do not go into colloidal solution by themselves may be induced to do so on adding particles that readily form a colloidal solution. An explanation of this may now be given. The *complete* precipitation of the particles from a solution means first of all that the particles gradually increase in size through combination. This gives rise to a gradual increase in concentration of the particles at the bottom of the vessel in comparison with that in the surface of the solution, according to equation (2). Ultimately a precipitate will be formed in the way already explained. Finally practically no particles will be in solution on account of their size. Hence if particles which by themselves readily go into solution keep in suspension particles which by themselves do not go into solution, the following state of affairs probably exists. A particle of the former kind on encountering one of the latter will not combine with it, since the former particle has a sphere of action associated with it extending into the liquid. If however, two particles of the latter kind encounter each other they would combine. But they may separate again in time through encounters with other particles, the chance of that happening depending on the number of other particles present. Thus the presence of particles which unaided remain in solution might have the effect of keeping the complexity of aggregations of particles of the other kind below a certain average degree, and thus prevent a precipitation of the latter particles. The effectiveness of this will evidently depend on the relative concentrations of the two different kinds of particles, and the total concentration of the particles. The fact mentioned that the flint and feldspar particles of porcelain slip are more or less kept in suspension by the clay particles, and that a precipitate obtained on adding a substance may be made to go into solution again through the addition of particles, are well explained in this way.

General Electric Co.,
Schenectady, N. Y.

THE HALL, ETTINGSHAUSEN, NERNST AND LEDUC EFFECTS IN CADMIUM, NICKEL AND ZINC.

By A. E. Caswell.

Synopsis.

Transverse Magnetic Effects in Cadmium, Nickel and Zinc.—The Hall, Ettingshausen, Nernst and Leduc effects were all measured for each metal on the same thin strip, which after being provided with various thermocouples and potential wires was heated electrically in vacuum and placed in a magnetic field of 4,000 to 5,200 gauss. Coefficients are given for cadmium (40 to 50°), nickel (− 11 to 57°) and zinc (− 25 to 77°). The Hall and Ettingshausen effects were not found of opposite sign as has usually been observed, but both came out positive.

SINCE the thermoelectric, galvanomagnetic and thermomagnetic effects observed in metals have not been determined for the same specimens and since these properties vary considerably in different specimens of the same substance the writer undertook to construct an apparatus with which to measure the transverse magnetic effects and the thermoelectric effects in the same specimen over a wide range of temperatures. So far he has been unable to determine the thermoelectric effects, especially the Thomson, with any degree of accuracy for any specimen sufficiently thin to give satisfactory results for the magnetic effects.

A considerable part of the work has been done under the auspices of the National Research Council in the Palmer Physical Laboratory of Princeton University. The writer takes pleasure in acknowledging his indebtedness to Dean Magie, who very kindly placed all the resources of the Laboratory at his disposal, and in expressing his deep appreciation of the uniform courtesy and generous coöperation shown him by all the members of the Princeton staff.

In the following paragraphs the most reliable results obtained for the transverse mangetic effects are given, being comparable in accuracy with the better results published elsewhere. Moreover, the published data are somewhat meager.

The specimens used were rolled to a uniform thickness of 0.01035 cm. from sticks of Kahlbaum's c. p. reagent cadmium, and of Kahlbaum's c. p. I zinc, and sheets of c. p. nickel. They were 1.2 cm. in breadth and 4.2 cm. in length, being firmly held at the ends by copper clamps through which the primary currents of electricity and heat were led into and out of the specimens. Four copper-constantan thermocouples were attached at intervals of 1.2 cm. along the longitudinal axis of the specimen, and two others were attached at the centers of its upper and lower edges. By means of these the temperatures of different points on the specimen were determined, the copper wires of the thermocouples being also used to determine electric potential differences. The thermoelements were used with a potentiometer reading to one-twentieth of a microvolt, the galvanometer being a Leeds-Northrup High Sensitivity Type R. The specimen, together with its clamps, was placed within an evacuated tube connecting two flasks of the Dewar type in which liquids could be placed with which to maintain steady temperature conditions. The tube was placed between the poles of a large Pye electromagnet by means of which fields were produced ranging from about 4000 to 5200 gauss.

In order to reduce the loss of heat through the thermocouples these were made of No. 44 copper and No. 34 constantan wire.

The results obtained are collected in Table I; R, P, Q and S being, respectively, the coefficients of the Hall, Ettingshausen, Nernst and Leduc effects. The Hall coefficient is defined by the equation $E = R(HI/D)$, where H is the intensity of the magnetic field in gausses, I is the primary electric current through the specimen in amperes, D is the thickness of the specimen in cm., and E is the resulting electric difference in potential between the two edges expressed in volts. Similarly, the Ettingshausen coefficient is given by the equation $T = P(HI/D)$, where T is the resulting temperature difference between the edges expressed in degrees Centigrade. The coefficient of the Nernst effect is given by $E = QHB(dt/dx)$, where B is the breadth of the specimen in cm. and dt/dx is the primary temperature gradient. The coefficient of the Leduc effect is given by $T = SHB(dt/dx)$, the symbols having the same significance as before. The sign of these effects is taken as positive when, the magnetic field being directed away from the observer and the primary current of heat or electricity flowing from left to right, the upper edge of the specimen is at the higher temperature or potential.

TABLE I.

Hall Effect.		**Ettingshausen Effect.**		**Nernst Effect.**		**Leduc Effect.**	
Temp. °C.	$R \times 10^{13}$.	**Temp. C.**	$P \times 10^{8}$.	**Temp. °C.**	$Q \times 10^{12}$.	**Temp. °C.**	$S \times 10^{7}$.
			Cadmium.				
+42.0	+ 8.50	+51.2	+5.96	+39.4	0	+39.4	− 1.87
+49.3	+ 11.67						

Nickel.

+57.2	+770.7	+55.8	+3.67	−11.4	+ 8.36	−11.8	0
				+37.6	+ 27.47	+38.9	−10.17

Zinc.

−24.7	+ 15.33	−17.1	0	−16.2	+290.0	−16.2	+37.59
+25.5	+ 8.20	+45.2	+1.76	+37.2	− 6.25	+37.2	+ 4.00
+32.6	+ 8.38	+60.7	+2.27				
+39.9	+ 8.18	+76.7	+3.02				
+41.2	+ 8.23						
+76.7	+ 9.82						

University of Oregon,
Eugene, Oregon,
March, 1922.

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PHYSICAL REVIEW.

THEORY OF IONIZATION BY CUMULATIVE ACTION AND THE LOW VOLTAGE ARC.

By Karl T. Compton.

Synopsis.

Theory of Ionization by Cumulative Action of Successive Impacts by Electrons and by Quanta of Resonance Radiation.—The phenomena of the low-voltage arc seem to require, for their explanation, ionization of the gas molecules in two (or more) successive stages. In the theory here developed it is supposed that each electron from the cathode after falling through a minimum potential difference reaches an active zone in which it collides either with a neutral molecule and partially ionizes it or with a partially ionized molecule which thereby becomes completely ionized. Each molecule when partially ionized emits a quantum of resonance radiation and this may go off in any direction and will in a short distance be absorbed by a neutral molecule which thereby becomes partially ionized and emits another quantum of radiation. So the passage through the gas of the quanta of resonance radiation initially set free by electronic impacts is analogous to the diffusion of foreign gas molecules. *Equations for the case of coaxial cylindrical electrodes* are derived for the proportion of molecules partially ionized (1) by direct impact and (2) by resonance radiation in terms of quantities which can all be readily measured except τ the mean life of the ionized molecules and $1/\rho$ the scattering coefficient for the radiation, for which (except ρ for mercury) only upper and lower limits can be estimated. The substitution of experimentally determined values leads to the conclusion that, under normal circumstances, partial ionization by photo-impact is many times as great as that by electronic impact alone and is necessary and sufficient to account for the observed ionization. The possibility of complete ionization by successive photo-impacts alone is also discussed.

Theory of Low-voltage Arc.—If n_0 is the number of electrons emitted and P_0 is the proportion of partially ionized molecules in the active zone, n_0P_0 is the number of molecules ionized per second. Since the positive ions move more slowly than electrons, each positive ion neutralizes the space charge due to $4\sqrt{(2 \times 1840M)}$ electrons; hence the electronic current increases to $1/(1 - 242P_0\sqrt{M})$ times the value it would have without ionization, provided the current is limited by the space charge around the cathode. As P_0 is increased by increasing the temperature of the filament or the applied potential, the current first increases to the saturation thermionic current, then the negative space charge is replaced by a positive space charge, the potential drop becomes concentrated near the cathode, the temperature of the cathode is raised by bombardment by positive ions, increasing n_0 and hence P_0; as a result the current increases at an accelerated rate, instability is usually soon reached and the arc strikes suddenly. The chief function of the gas is to give the

positive space charge around the cathode which is the distinguishing feature of the arc. If n is the saturation value of thermionic emission, the maximum current will be $3/2ne$ or $2ne$ depending on whether the voltage is below or above the minimum ionizing potential.

Low-voltage Arc in Mercury Vapor.*—Recent experiments indicate that the *striking voltage* is about 5.6 instead of 4.9 volts, and that the arc may be dependent on either the 4.9 volt (2536 Å.) or the 6.7 volt (1849 Å.) radiation according to the age of the vapor. Thus there seem to be *two meta-stable states of the neutral mercury atom.

***Theory of Temperature of Ionization of Gases.*—It is pointed out that resonance radiation must also be the chief factor in temperature ionization both in the electric furnace and in the sun and other stars.**

1. INTRODUCTION.

IN two recent papers the writer emphasized the impossibility of explaining low voltage arcs by ionization of gas molecules by single electron impacts.[1] By a low voltage arc, is meant one which strikes and operates at a voltage less than the minimum ionizing potential of the gas. The phenomena seem to demand, for their explanation, ionization of gas molecules in successive stages by two or more separate agents. Hughes has suggested the name "cumulative ionization" to describe such effects and has given a survey of the subject in his recent Report on Photoelectricity.[2] Cumulative action is probably an important factor also in temperature ionization, but it is in the low voltage arc that it can be most easily investigated.

There are three possible processes of cumulative ionization which seem reasonable in the light of our present knowledge: (1) Ionization by Successive Impact; (2) Photo-Impact Ionization; (3) Ionization by Successive Photoelectric Action. In the first of the writer's earlier papers an attempt was made to test the first of these possibilities. The equations there derived, however, are not accurately applicable to actual experimental conditions, so that the conclusions reached in the former paper must be considered as quite tentative. In the present paper the first two of these processes are tested by comparing the amount of ionization observed experimentally with the amount predicted by each of the processes under the conditions of the experiment. While there is uncertainty regarding the magnitude of several quantities appearing in the equations, yet the argument leads to some important and fairly definite conclusions.

2. (*a*) TOTAL CURRENT IN ABSENCE OF ARC.

Let Fig. 1 represent a discharge tube, in which A is the anode and C is the incandescent cathode which emits the electrons whose impacts against gas molecules may result in their complete or partial ionization. If the applied accelerating potential difference V exceeds the minimum radiating potential V_r of the gas, there will be inelastic collisions, and partial ionization of some of the molecules, together with emission of resonance radiation, will occur. Let the shaded area represent the region in which, on the average, these effective impacts occur. As a result of these collisions, suppose a fraction P of the molecules in this shaded region to be in a partially ionized state, capable of being completely ionized by the impact of any electron which has not yet lost its energy. If n electrons leave the cathode, then Pn is the resulting amount of ionization.

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[1] PHYS. REV., 15, p. 476, 1920; Phil. Mag., 43, p. 531, 1922.

[2] National Research Council Bull., Vol. 2, No. 10.

Each molecule thus ionized adds to the total current in two ways: (1) by contributing two additional ions, and (2) by the effect of the relatively slowly moving positive ions in neutralizing some of the space charge around the filament and thus permitting the escape of more electrons from it. These additional electrons may also be effective in producing further ionization, which will liberate more electrons, and so on. The total resulting current can thus be expressed as the sum of an infinite number of terms, forming a converging series, which can readily be expressed in a simple form as follows.

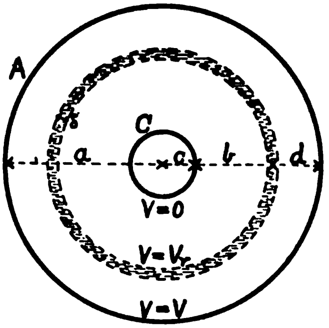

Fig. 1.

Each positive ion is drawn toward the cathode, through the outward stream of emitted electrons, and both make numerous collisions with molecules, since the phenomena in which we are interested are important only provided the mean free path is small in comparison with the distance between the electrodes. The average rate of motion of an ion through the gas is proportional to $\lambda\bar{c}$, where λ is its mean free path and $\bar{c}$ is its average velocity. The mean free path of the electrons is $4\sqrt{2}$ times greater than that of the ions and their average velocity is $\sqrt{1840M}$ times greater, where M is the molecular weight on the basis of 1 for the hydrogen atom. Thus each positive ion remains in the region of the negative space charge $4\sqrt{3680M}$ times as long as an escaping electron, neutralizes the space charge of that number of electrons and permits that number to escape from the cathode. Furthermore, as will be shown later, the probability P of partial ionization of a molecule in the shaded region is necessarily proportional to the number of bombarding electrons.

Let n_0 be the number of electrons which would leave the cathode if there were no ionization. Due to these, a fraction P_0 of the molecules in the shaded region are partially ionized and the resulting number of molecules completely ionized is n_0P_0. This number of positive ions liberates $4\sqrt{3680M}n_0P_0$ additional electrons from the cathode. Thus

$$n' = n_0(1 + 4\sqrt{3680M}P_0)$$

electrons would leave the cathode if only the original n_0 could ionize. Putting, for the present, $4\sqrt{3680M}P_0 = Cn_0$, we have

$$n' = n_0(1 + Cn_0).$$

But, if we include the effect of ionization due to those electrons liberated by positive ions produced by the n_0 electrons, we have

$$n'' = n_0(1 + Cn') = n_0(1 + Cn_0 + C^2n_0^2).$$

Similarly

$$n''' = n_0(1 + Cn'') = n_0(1 + Cn_0 + C^2n_0^2 + C^3n_0^3)$$

is the number of emitted electrons if we include ionization due to all the n'' electrons. The actual total number of electrons leaving the cathode is seen to be

$$n = n_0(1 + Cn_0 + C^2n_0^2 + \cdots) = \frac{n_0}{1 - Cn_0}.$$

Thus we have

$$n = \frac{n_0}{1 - 4\sqrt{3680M}P_0}, \tag{1}$$

provided the current is limited by the negative space charge around the cathode.

It is easily possible to measure n and to calculate n_0 by the relation[1] $n_0 \propto V^{3/2}$, determining the constant of proportionality by measurements of n at values of V less than V_r, where n and n_0 are identical. Thus equation (1) enables definite values of P to be determined under definite experimental conditions and permits a quantitative test of the values of P predicted by the theories of ionization by successive impact and photo-impact ionization to be outlined later.

Incidentally, this equation offers an explanation of the striking of an arc. As P_0 is increased, by increasing n_0 or the applied potential, n increases more and more rapidly and would become infinite when

$$P_0 = 1/4\sqrt{3680M}$$

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[1] Langmuir, PHYS. REV., 2, p. 402, 1913.

were it not limited to the value corresponding to the saturation thermionic current at the temperature of the cathode. The number of available electrons being thus limited, the negative space charge becomes neutralized and is finally replaced by a positive space charge as the voltage is raised. As the space charge becomes positive, the potential drop becomes concentrated near the cathode, so that the electrons attain their critical speed within a short distance of the cathode. This concentration of the region of effective impacts tends further to increase the probability of cumulative ionization, measured by P. At the same time the temperature of the cathode is raised by the bombardment of the positive ions, which increases n_0 and P_0. Thus, after ionization sets in, the current increases at an accelerated rate as the voltage is raised. This increase may be slow or rapid, depending on the value of n_0, so that the setting in of the arc may be made gradual enough to be experimentally followed in all of its stages. Usually, however, the conditions near the arcing voltage are such that P_0 spontaneously increases as a result of the more favorable distribution of potential and the increase in the cathode temperature, so that a point of instability is reached at which the arc strikes suddenly,—the further increase of current occurring spontaneously. In any case the presence of a positive space charge around the cathode is the distinguishing feature of an arc.

2. (*b*) Total Current in Arc.

If the arc is operating at a voltage a little larger than the minimum ionizing potential V_i, the maximum current is obtained if each of the n electrons emitted from the cathode ionizes a molecule, so that the total current is $(n + n)e = 2ne$.

If the arc operates at a voltage between the minimum radiating potential V_r and the minimum ionizing potential V_i, the maximum possible current occurs when half of the n electrons collide to partially ionize molecules and the other half complete the process of ionization. Thus, in the low voltage arc, the maximum current is $(n + n/2)e = 3/2ne$. In both cases n is the saturation value of thermionic emission from the cathode at its temperature.

Recombinations would diminish the above values somewhat. Probably this decrease due to recombination is not large in the case of an intense arc, since each loss by recombination liberates radiant energy which may contribute to another ionization, and since the ionization occurs close to the cathode so that there is only a small region in which electrons and positive ions exist together.

Thus the chief function of the gas in a low voltage arc is to give a positive space charge around the cathode, causing sufficient potential gradient to give a saturation current with low voltages, and to raise the cathode temperature by ionic bombardments and thus increase the saturation current.

The foregoing conclusions have received very satisfactory experimental support, which will be discussed in a later paper.

3. THEORY OF IONIZATION BY SUCCESSIVE IMPACTS.

The n electrons per second from the filament are drawn through the gas and attain a speed corresponding to the minimum radiating potential V_r. Each will lose its energy at some subsequent impact and partially or completely ionize the impacted molecule, according as the molecule was in the normal or partially ionized state before impact. Let τ be the average interval of time during which a molecule remains partially ionized, *i.e.*, the average interval between excitation and radiation. If δ is the thickness and f the length of the layer within which, on the average, these effective impacts occur, and if a fraction P of the molecules are partially ionized at any instant, then $n(1 - P)$ molecules are partially ionized each second. The aggregate time of activation of all molecules partially ionized in the layer δ per second is $n(1 - P)\tau$. This, divided by the number of molecules in the layer, gives the fraction of the molecules in the region of effective impacts which are, at any instant, in the partially ionized state as the result of a direct electron impact. Calling this P_i, we have

$$P_i = \frac{n(1 - P)\tau}{vNp},$$

where p is the gas pressure, N the number of gas molecules per unit volume at unit pressure and v the volume of the layer in which effective impacts occur. If the electrodes are coaxial cylinders, as in Fig. 1, $v = 2\pi(b + c)f\delta$.

Furthermore, P is always very small compared with unity unless the arc has already struck, as is evident from equation (1). Under these conditions

$$P_i = \frac{n\tau}{2\pi(b + c)f\delta Np}. \tag{2}$$

In order to apply this equation it is necessary to know $(b + c)$ and δ. Simple consideration of the distribution of potential (see Fig. 1) shows that

$$(b + c) = a\epsilon^{-\frac{V-V_r}{V}\log\frac{a}{c}}, \tag{3}$$

where a and c are the respective radii of anode and cathode.

The calculation of δ is more difficult, for it depends on the average distance which the electrons move beyond the point at which they have acquired energy eV_r before making an effective impact, and also on the distribution of velocities of electrons which causes them to gain the critical energy at different distances from the cathode.

Suppose, first, that all n electrons are emitted from the cathode with the same speed. Since all collisions at speeds less than the minimum radiating speed are perfectly elastic, they all attain this critical speed at the equipotential surface V_r whose position we shall specify by $x = 0$.

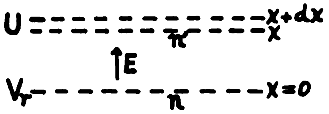

Fig. 2.

$$\nu = \frac{4rUp^2}{El^2} \tag{4}$$

is the number of collisions made by an electron, whose mean free path in the gas at unit pressure is l, in advancing unit distance.[1] E is the electric intensity and r is a numerical factor whose value lies between 0.87 and unity, and which may be neglected in our present work. If n' out of the n electrons reach the surface x, at potential U, without having lost their energy at an intervening impact, then $n'\nu dx$ of these will collide in the ensuing layer of thickness dx. The probability that any one of these impacts will be effective in activating a molecule is known to be, at least approximately, of the form $(U - V_r)/V_r = Ex/V_r$.[2] Thus the decrease in n' in passing through the layer dx is

$$dn' = -\frac{E}{V_r}\nu n' x dx,$$

whence

$$n' = n\epsilon^{-\frac{E\nu x^2}{2V_r}}.$$

The average distance which the electrons go beyond the surface V_r before colliding effectively is xdn'/n, integrated over all possible values of x, or

$$\bar{x} = \int_0^\infty \frac{E}{V_r}\nu x^2 \epsilon^{-\frac{E\nu x^2}{2V_r}} dx.$$

When this expression is integrated, and the value of ν substituted from equation (4), we find

$$\bar{x} = \sqrt{\frac{\pi}{8}}\frac{l}{p}, \tag{5}$$

which is about two thirds of the electronic mean free path.

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[1] Benade and Compton, Phys. Rev., 11, p. 194, 1918.

[2] Compton, Phys. Rev., 15, p. 482, 1920.

This expression would give the appropriate value of δ (to at least the right order of magnitude) if all electrons left the cathode with equal speeds. Actually, however, they have initial speeds distributed approximately according to Maxwell's Law, and with an average energy $e\bar{V} = \alpha T$ characteristic of gas molecules at the temperature of the cathode.[1]

Thus the electrons, on the average, attain their critical energy eV_r within a layer whose thickness is $\delta' = \bar{V}/E$. Since this layer is distant $(b + c)$ from the axis,

$$E = \frac{V}{(b + c) \log a/c} \cdot$$

Therefore,

$$\delta' = \frac{\alpha T}{eV}(b + c) \log \frac{a}{c} \cdot \tag{6}$$

The value of δ, at least to a close approximation, is given by the sum of equations (5) and (6). An idea of the magnitude of $\bar{x}$ and δ' is obtained from the following calculations for mercury and helium, which have extremely small and large values, respectively, of the electronic mean free path.

TABLE I.

For Hg : $l = 0.0133$ cm.; $V_r = 4.9$ volts.
He : $l = 0.1175$ cm.; $V_r = 20.4$ volts.
Take $V = V_r + 1$, $a = 0.5$ cm., $c = 0.025$ cm.

p (mm.).	$\bar{x}$ (cm.).		$T°$ K.	δ' (cm.).	
	Hg.	He.		Hg.	He.
1	0.0083	0.0732	2000	0.0375	0.0150
2	0.0041	0.0366	2500	0.0470	0.0187
10	0.0008	0.0073	3000	0.0561	0.0225

It is seen that δ' is more important than $\bar{x}$ except at low pressures, particularly in the case of the heavier elements.

Returning to equation (2), we have for the final expression

$$P_i = \frac{n\tau}{2\pi(b + c)fNp\left\{\sqrt{\frac{\pi l}{8p}} + \frac{\alpha T}{eV}(b + c) \log \frac{a}{c}\right\}}, \tag{7}$$

in which $(b + c)$ is given by equation (3). All quantities appearing here are known or can easily be measured except τ, which may tentatively be assigned a value of probably the right order of magnitude.

4. THEORY OF PHOTO-IMPACT IONIZATION.

On this theory, impacts in the shaded layer produce resonance radiation which is absorbed and reëmitted by atom after atom before escaping from the gas, so that, as a result of each atom which is "activated" by a direct impact, many others are indirectly activated through absorption of radiation. Thus the probability P_r that an atom in the shaded region of effective impacts is in a partially ionized condition as a result of absorbed radiation is greater than the probability P_i of activation by direct impact. Our problem is to derive an expression for P_r.

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[1] Sih Ling Ting, Roy. Soc. Proc. A., 98, p. 374, 1921.

It will be seen that the passage of radiation of the resonance type through the gas may be handled by expressions of the same type used to describe the diffusion of ions or of foreign molecules through a gas. A beam of light, passing through an absorbing or scattering medium falls off in intensity according to the law $I = I_0\epsilon^{-\alpha/x}$, where α is the absorption coefficient. A stream of particles passing through a gas is reduced by collisions, or scattering, according to the law $n = n_0\epsilon^{-x/l}$, where l is the mean free path. By analogy, let us call λ the mean free path of the radiation, defining it as the reciprocal of the absorption coefficient, or the distance in which the intensity of a beam falls to $1/\epsilon$ of its value as a result of resonance scattering. Then the average speed of the radiation $\bar{c}$ is this distance λ divided by the time of "activation" τ. We may then apply the diffusion equation

$$\int\int\frac{1}{3}\lambda\bar{c}\,\frac{\partial N'}{\partial n}\,dS = -\int\int\int R\,dx\,dy\,dz, \qquad (8)$$

where N' is the number of activated atoms per unit volume at any point in the gas, R is the net rate at which atoms are becoming activated by direct electron impacts and n is the outward normal to the closed surface over which the surface integral and within which the volume integral are taken.

This equation may have a mere formal, and not a physical, similarity to the case of diffusion of particles. However, there are grounds for quantelizing the radiant energy in units of magnitude $h\nu$, since it is known that this amount of energy is absorbed by an atom in becoming "activated" and it must be emitted again when the atom radiates and returns to the normal state. In this case the mean free path λ may be physically similar to the mean free path of a gas molecule. However this may be, it seems safe to use equation (8) to calculate N', which is our purpose.

Referring to Fig. 1, $n(1 - P)$ quanta of resonance radiation are produced by electron impacts each second in the cylindrical layer of radius $(b + c)$, length f and thickness δ. Some of this radiation diffuses toward the anode and some toward the cathode. Let the corresponding numbers of quanta be $n_a(1 - P)$ and $n_c(1 - P)$, respectively. There will be one cylindrical surface within the layer δ across which the net radiation flux will be zero and which we may call the neutral surface. If we apply equation (8) to the region bounded by this surface and a co-axial surface of radius r, lying outside the neutral surface, we have

$$\frac{1}{3}\lambda\bar{c}\frac{dN'}{dr}(2\pi rf) = -n_a(1-P);$$

whence

$$N_a' = -\frac{3n_a(1-P)}{2\pi f\lambda\bar{c}}\log r + C_a$$

is the value of N' at any point outside the neutral surface, distant r from the axis. If the reflecting power of the electrodes for resonance radiation is negligibly small, as is approximately the case for most substances, $N_a' = 0$ when $r = a$, so that

$$N_a' = \frac{3n_a(1-P)}{2\pi f\lambda\bar{c}}\log\frac{a}{r}.$$

Similarly, at points inside the neutral surface,

$$N_c' = \frac{3n_c(1-P)}{2\pi f\lambda\bar{c}}\log\frac{r}{c}.$$

We have $n_a + n_c = n$ and at the neutral surface $r = (b + c)$ we have $N_a' = N_c' = N'$. From these relations it is easily shown that, at the neutral surface,

$$N' = \frac{3n(1-P)}{2\pi f\lambda\bar{c}}\,\frac{\log\dfrac{a}{b+c}\log\dfrac{b+c}{c}}{\log\dfrac{a}{c}}. \tag{9}$$

We implicitly assumed, in deriving this, that the thickness δ is negligible in comparison with the distance between the electrodes. This is nearly enough true in cases where low voltage arcs can be obtained. If the reflecting power of the electrodes for resonance radiation were considerable, equation (9) would take a more complicated form. It should, however, give results of the right order of magnitude in the cases to which we wish to apply it.

If the space charge around the cathode is negative, and if the voltage V is not much larger than V_r, then the critical layer δ is near the anode and we may replace a by $(b + c)$ in the denominator, so that

$$N' = \frac{3n(1-P)}{2\pi f\lambda\bar{c}}\log\frac{a}{b+c}.$$

Substituting for $(b + c)$ from equation (3) we have

$$N' = \frac{3n(1-P)}{2\pi f\lambda\bar{c}}\,\frac{V-V_r}{V}\log\frac{a}{c}. \tag{10}$$

If $1/\rho$ is the scattering coefficient of the gas at unit pressure for the resonance radiation, *i.e.*, ρ is the distance in which the intensity of a beam would fall to $1/\epsilon$ of its value, then p/ρ is the scattering coefficient at pressure p. If a fraction P of the atoms are partially ionized, and therefore unable to absorb resonance radiation, we have

$$\lambda = \frac{\rho}{p(1 - P)} \tag{11}$$

as the definition of the effective mean free path λ of the radiation. Putting $\bar{c} = \lambda/\tau$, we have

$$N' = \frac{3p^2 n\tau}{2\pi f\rho^2} \frac{V - V_r}{V} \log\frac{a}{c}, \tag{12}$$

since the factor $(1 - P)^3$ may be neglected owing to the small value of P possible by equation (1).

We can now derive P_r, the fraction of atoms in an activated state because of absorbed resonance radiation, for $P_r = N'/Np$, where Np is the number of molecules per unit volume. Thus, finally,

$$P_r = \frac{3pn\tau}{2\pi fN\rho^2} \frac{V - V_r}{V} \log\frac{a}{c}. \tag{13}$$

5. Importance of P_i and P_r.

The total probability of partial ionization in the region of effective impacts is $P = P_i + P_r$. It is found that P_r is much larger than P_i under conditions in which low voltage arcs are obtained, for

$$\frac{P_r}{P_i} = \frac{3p^2(b + c)\delta}{\rho^2} \frac{V - V_r}{V} \log\frac{a}{c}.$$

δ is the sum of $\bar{x}$ and δ' and is seen, in Table I., to be of the order of 0.01. $(b + c) \log a/c$ is of the order of unity in ordinary apparatus. If the arc strikes at about 0.1 volt above the minimum radiating potential, $(V - V_r)/V$ is of the order of 0.01. The pressures range from 0.5 to 10 mm. R. W. Wood[1] gives data from which ρ may be calculated to be 0.000675 cm. for the 2536 line of mercury vapor. Lamb[2] gives a very general law of resonance scattering, applicable if *every* molecule possesses an oscillator of proper frequency, from which it is readily shown that

$$\rho = \frac{1.54}{N\lambda_r^2}, \tag{14}$$

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[1] Recent Researches in Physical Optics.

[2] Camb. Phil. Soc. Trans., 18, Stokes Commemoration, 1900.

where λ_r is the wave-length of the resonance radiation. This gives a minimum possible value of ρ which, in the case of the mercury 2536 line, is 10,200 times smaller than the experimental value, indicating that not all the molecules contain this type of oscillator or that their natural frequencies are distributed over a sufficient frequency range to account for the discrepancy. As far as the writer is aware, ρ has not been experimentally determined in any case except for the mercury 2536 radiation.

Using the experimental value of ρ for mercury, it is found that the ratio P_r/P_i is of the order of 10,000. Under any ordinary conditions, therefore, the direct effect of impacts is negligible in comparison with the indirect effect due to radiation in producing partially ionized atoms, capable of ionization by a low velocity impact.

The above comparison is possible without any knowledge of the time interval τ or the magnitude of the thermionic current. It is of interest, also, to see whether the probable *absolute* values of P_r or P_i are of the right order of magnitude to explain the size of the currents at which low voltage arcs are observed to strike.

Take the following reasonable values for the quantities involved. $a = 0.5$ cm., $c = 0.025$ cm. (20 mil wire), $f = 1$ cm. give the dimensions of the apparatus. $V_r = 4.9$ volts, $l = 0.0133$ cm. for mercury and $V_r = 20.4$ volts, $l = 0.1175$ cm. for helium are definite constants, as are also $N=3.6(10)^{16}$ per c.c., $\alpha=2(10)^{-16}$ ergs/degree and $e=4.77(10)^{-10}$ e.s.u. $V = V_r + 1$ is a striking voltage for an arc in mercury or helium which is very easily realized with only moderate thermionic currents.

$\tau = 6(10)^{-7}$ sec. is the most favorable experimental value determined for any substance.[1] It was found for the D_3 line of helium. No determination of τ for a resonance line has ever been made. This is the most uncertain value entering into the calculations. $n = 1.84(10)^{14}V^{3/2}$, where V is in volts, gives the largest (hence most favorable) possible thermionic current. This is calculated from Langmuir's formula for the current limited by space charge in *vacuo*. Actually the current is less than this, since the presence of gas around the cathode reduces the rate of escape of electrons and thus increases the space charge for a given number of electrons. Furthermore, it is found experimentally that the currents need not be nearly so large as this to produce an arc at $V = V_r + 1$. Nevertheless, take this as the most favorable possible value.

$\rho = 0.000675$ cm. for mercury vapor, and is unknown, but probably smaller, for helium.

Substitution of these values in equation (7) for P_i gives the results in Table II.

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[1] Stark, Ann. d. Phys., 49, p. 731, 1916.

TABLE II.

Values of P_i.

p (mm.).	$T°$ K.	Hg.	He.
1	2000	5.1 $(10)^{-7}$	12.6 $(10)^{-7}$
2		2.8	10.8
10		0.6	5.0
1	2500	4.7	12.1
2		2.6	10.0
10		0.55	4.2
1	3000	4.1	11.6
2		2.2	9.4
10		0.46	3.7

If these results are substituted in equation (1) we find n/n_0, or the ratio in which ionization has increased the total current just before the striking of the arc, as shown in Table III.

TABLE III.

Values of n/n_0.

p (mm.).	$T°$ K.	Hg.	He.
1	2000	1.00177	1.00061
2		1.00096	1.00052
10		1.00021	1.00024
1	2500	1.00161	1.00059
2		1.00089	1.00048
10		1.00019	1.00020
1	3000	1.00141	1.00056
2		1.00075	1.00045
10		1.00016	1.00018

These values are entirely inadequate to account for the experimentally observed values of n/n_0, which may range, roughly, from 2 to 100. Furthermore, they indicate variation both with pressure and temperature which is in a direction opposite to that observed.

R. W. Wood[1] has recently shown that, in the *excitation of fluorescence* of mercury vapor by light of wave-length 1850–2100 Å., there is a definite time interval of 1/15,000 second between the absorption of the light and the subsequent bursting into luminosity by the vapor. If this is the time interval which is effective in the present problem, we should put

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[1] Roy. Soc. Proc. A., 99, p. 362, 1921.

$\tau = 6.7(10)^{-5}$ sec., which is about 110 times larger than the value assumed above. Substitution of this quantity gives values of P_i for mercury ranging between $5.6(10)^{-5}$ and $0.5(10)^{-5}$ and values of n/n_0 between 1.24 and 1.02 in the above tables. These values approach in magnitude the observed values of n/n_0, but are still too small. Furthermore, the assumed maximum value of n is about 200 times larger than actual values of n at which low voltage arcs can be obtained in mercury vapor. Taking this into account it seems as if the values of n/n_0 in Table III. represent the predictions of the Theory of Successive Impacts fairly accurately. In any case the indications are that successive impacts play a relatively insignificant part in cumulative ionization.

Turning now to photo-impact ionization and substituting the above values in equation (13) for P_r, we find $P_r = 0.055p$ in the case of mercury vapor. No calculation can be made for helium because of lack of knowledge of ρ. At pressures at which a low voltage arc will strike in mercury, *i.e.*, above about 0.15 mm., this value of P_r is more than sufficient to cause the arc to strike, as indicated by putting $n/n_0 = \infty$ in equation (1). For instance, at 1 mm. pressure, the calculated value is about 180 times as large as necessary to produce the arc. In other words, the theory would predict an arc at a thermionic current at least 180 times less than the maximum possible current which was assumed above. This is in good agreement with observations in an experiment, still in progress, by Mr. Y. T. Yao and the writer. 1/180 part of the value of n assumed above is $1.46(10)^{13}$, which corresponds to a thermionic current of 2.2 micro-amperes. In an apparatus of the dimensions assumed above, and under approximately the assumed conditions, the arcs strike at currents of a few micro-amperes.

Thus it appears probable that the ionization observed in gases at voltages less than their minimum ionizing voltages is due chiefly to photo-impact ionization. We cannot say more than this until the constant τ is measured for the resonance radiation of those gases in which low voltage arcs can be obtained, *i.e.*, monatomic gases and vapors.[1]

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[1] *Note.*—Hughes has pointed out the fact that, in a gas whose minimum radiating potential is less than half the ionizing potential, no two cumulative effects at this voltage could contribute sufficient energy for ionization. The experiments of Mr. Yao and the writer indicate, however, that proper corrections for velocity distribution place the striking voltage of the low voltage arc in mercury at about 5.6 volts, instead of 4.9 volts. Thus the electron impact against the partially ionized atom must contribute an amount of energy sufficient to increase the total potential energy to the value required for ionization, as demanded by theory. Furthermore, experiments to be later described by Mr. Yao indicate that the low voltage arc in mercury may be dependent on either the 4.9 volt (2356) or the 6.7 volt (1849) radiation according to whether the vapor is in close or distant communication with its liquid surface. This and spectroscopic evidence suggests two meta-stable states of the neutral mercury atom. Thus the actual conditions are somewhat more complicated than those assumed in the theory.

6. Ionization by Successive Photoelectric Action.

F. Horton and Miss A. C. Davies have recently suggested that the second stage in the process of ionization may also be accomplished by the absorption of radiation from neighboring impacts.[1] Their experimental results with helium prove the diffusion of resonance radiation through the gas, the existence of photo-impact ionization and, apparently, the existence of ionization by photoelectric action on atoms which are already partially ionized by absorption of radiation. If there exists a second type of resonance radiation which is capable of ionizing atoms which have partially absorbed the first type, or if the resonance potential exceeds half the ionizing potential, we should expect this radiation to be more effective than electron impacts in completing ionization, for the same reason that radiation is more effective than impacts in producing the first stage of ionization. An attempt to reduce this type of ionization to quantitative form led to some suggestive results, but the equations become so complicated and the relation of the second photoelectric process to the first involves such uncertain hypotheses that it will not be discussed here. The importance of this type of ionization, which seems proved in the case of helium, can probably best be established in the case of metallic vapors by direct experiment or by a proven inadequacy of the two alternative processes discussed in this paper.

7. Discussion.

The chief result which seems to emerge definitely from the above discussion is that resonance radiation plays a very important part in ionization at low voltages. At high voltages and low gas pressures, as in the Geissler tube discharge, there is good opportunity for ionization by direct single impacts. But if the potential drop in the distance of a mean free path is much less than the ionizing potential, conditions are unfavorable for direct ionization and the cumulative type of ionization preponderates.

If we carry conditions a step further in the same direction we have the case of purely temperature ionization, in which there is no potential drop at all. Here, presumably, cumulative ionization is practically the only type and resonance radiation is an essential agent in the process.

This concept has an interesting application to the case of ionization in the solar chromosphere, recently discussed by Saha.[2] He treats the chromosphere as an enclosure at constant temperature and uses Nernst's equation of the isobar to calculate the degree of ionization of any gas, treating ionization as a dissociation. This theory has been remarkably successful in explaining and predicting features of the solar spectrum. The theory fails, however, to explain the fact that, although sodium and barium have equal ionizing potentials, barium is much more completely ionized than is sodium. This may be explained, as has been pointed out by Professor H. N. Russell and the writer,[1] by taking account of the effect of resonance radiation of these elements. For the chromosphere is not an enclosure, but a layer through which is passing an enormous flux of energy from the hotter interior. Observation shows, and there are reasonable explanations of it, that this flux is particularly deficient in radiation of the resonance type for sodium,—much more deficient than in the corresponding radiation for barium. Thus neutral barium atoms must exist largely in the partially ionized state. This is equivalent to a relative lowering of the ionizing potential for barium, permitting more complete ionization.

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[1] Phil. Mag., 12, p. 746, 1921.

[2] Phil. Mag., 40, pp. 472, 809, 1920.

The spectral peculiarities of light excited in the low voltage arc (and also in the high temperature furnace) are necessary consequences of the mechanism of ionization here discussed. If the gas pressure is high and the electric field weak, so that the energy gained by an electron between collisions is small, there is little chance of exciting any radiation except that of the resonance type corresponding to the inelastic impact of lowest velocity. Thus we get the "single line" spectrum. If the pressure is less or the field greater, an appreciable number of electrons may attain speeds sufficient to excite a second type of resonance radiation of shorter wave-length. Such lines are the $1S - 1p$ and $1S - 1P$ lines of the alkaline earths. As a result of cumulative ionization, a complete spectrum will be present, but will be weak and will become, relatively to the resonance line or lines, of vanishingly small intensity as the voltage and current are diminished.

As soon as the arc strikes, conditions are at the other extreme. Owing to the positive space charge around the cathode, the electric intensity in this region is very large and the electrons are shot out into the gas with practically the maximum velocity attainable at the applied voltage. Then the resonance lines are not particularly "favored," and the entire arc spectrum appears. If the voltage is sufficiently large, the enhanced lines will appear. In fact, in this type of arc, there is realized somewhat the same distribution of potential which has been secured in a more manageable way by Foote, Meggers and Mohler[2] by the introduction of an additional gauze electrode near the cathode, and which has made possible their most interesting work on enhanced spectra.

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[1] Astrophys. Jour. (in print).

[2] Phil. Mag., 42, p. 1002, 1921.

In conclusion, mention should be made of a method of experimentally testing the above theories. The most decisive test of photo-impact ionization would be to illuminate a gas with its resonance radiation from an external source and see whether ionization can then be observed with electron impacts of velocity less than the ordinary minimum ionizing velocity. Such an effect has been observed in iodine vapor,[1] but this is a case of fluorescence and not true resonance—though the mechanism of ionization is probably similar. Last year, Mr. Yao made careful attempts to prove photo-impact ionization in this way with mercury and sodium vapors, but with results which were indecisive because of peculiar difficulties in getting intense resonance radiation of exactly the effective wave-length into a gas from an external source. These experiments are now being repeated under more favorable conditions.

Palmer Physical Laboratory,
Princeton, N. J.

Since this article was submitted, a very interesting paper by F. M. Kannenstine (Astrophys. Jour. 55, p. 345, 1922) has described a method of determining the time during which the metastable (partially ionized) helium atoms persist in a helium arc after the exciting voltage has been removed. The time is about 2.4 $(10)^{-3}$ second, which is much larger than the value of τ used above. If cumulative ionization is by successive impacts, then Kannenstine's value should be the value of τ for helium. If the ionization is of the photo-impact type, however, Kannenstine's measurements give the time required for the resonance radiation to escape from the region of effective impacts, which may include the time of many absorptions and reëmissions, and therefore τ would be much smaller than 2.4 $(10)^{-3}$. This point, and other recent evidence will be discussed briefly in another communication.

[1] Smyth and Compton, Phys. Rev., 16, p. 501, 1920.

THE THERMIONIC WORK FUNCTION OF TUNGSTEN.

BY C. DAVISSON AND L. H. GERMER.

SYNOPSIS.

Measurements of the Thermionic Work Function of Pure Tungsten have been made by two methods for the same segment of a uniformly heated filament simultaneously. The filament, of diameter 0.0755 mm. and with three finer tungsten leads welded to it 3.85 cm. apart, was kept stretched, by means of a molybdenum spring, between two molybdenum plates used to apply an electric field and to receive the space current, the ends of the filament being surrounded by guard boxes to limit the emission to the section of the filament between the potential leads. All parts were sealed inside a tube and so thoroughly out-gassed by alternately baking the tube and heating the metal parts that the residual pressure during the measurements was only about 10^{-7} mm., as measured with an ionization manometer. (1) In the *calorimetric method*, the equivalent voltage of the work function was computed from the relation $\varphi = 2EI(\Delta E/i)/(E - IdE/dI)$, where E is the voltage across the segment and I the current through it, and ΔE is the voltage change when the space current i flows from the filament, I being kept constant. Since ΔE was only from 10^{-3} to 10^{-4} times E, special precautions had to be taken to measure it with sufficient accuracy and to keep I sufficiently constant. Observations from 2070° K. to 2300° K. show an apparent increase for φ of about 2 per cent. in this range, considerably greater than is to be expected theoretically. At 2270° K., when correction is made for the asymmetry of the electric shielding (− 2.24 per cent.) and for the radiation from the plates heated by the space current (+ 4.12 per cent.), φ comes out 4.91 ± .05 volts. (2) In the *temperature variation method*, assuming Richardson's equation $\log i = \text{const.} + 1/2 \log T - \varphi e/kT$, measurements of the emission in the range 1930° to 2300° K. give for φ the values 4.87 or 4.78 volts according as the temperature scale of Langmuir or that of Worthing and Forsythe is adopted. The latter scale is probably more reliable but gives a value of φ 2.7 per cent. less than the value obtained calorimetrically, a difference believed to be greater than the probable error of the measurements.

Suggested Modification of the Theory of Conduction of Electricity in Metals.—The thermal energy of conduction electrons is supposed to be $3/2kT$ by the classical theory upon which the above computations of φ are based. If, however, the energy is taken to be practically zero then the same data lead to 4.52 and 4.48 volts for the values of φ by the two methods and the agreement is within the probable error of the measurements.

INTRODUCTION.

THE equation,

$$i = AT^{1/2}\epsilon^{-b/T}$$

proposed by Richardson[1] in 1902 to represent the current from a thermionic source as a function of temperature has been found to be of general and precise application within the limits of error of such measurements.

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[1] Camb. Phil. Soc. Proc., 11, p. 286 (1902). Phil. Mag. A, 201, p. 497 (1903).

This equation is a special form of the more general equation

$$i = AT^{1/2}\epsilon^{\int^{T}\frac{\omega}{kT^2}dT},$$

in which ω is the work required to liberate a single electron and k is Boltzmann's gas constant. The first equation is obtained from the second by assuming that ω is independent of T. The integral in the general equation can then be evaluated, and the relation takes the simpler form, in which $b = \omega/k$. It is customary to express ω as the product of a voltage times the electronic charge, $\omega = \varphi e$, so that $\varphi = kb/e$. This is referred to as the equivalent voltage of the work function.

The adequacy of the simpler equation might seem to justify the assumption regarding the independence of ω and T, and this, within limits, is true. It is well recognized, however, that on account of the particular form of the temperature-emission relation moderate variation in ω with temperature cannot be detected within the limits of accuracy ordinarily attained in such measurements. Thus, if $\omega = \omega_0(1 + \alpha T)$, the general equation reduces to

$$i = AT^{\left(\frac{1}{2}+\frac{\omega_0\alpha}{k}\right)}\epsilon^{-\frac{\omega_0}{kT}}$$

and the only hope of detecting the variation in ω is to distinguish between 1/2 and the true value of the exponent of T. This T factor is so unimportant compared with the exponential factor that its exponent cannot be determined with anything approaching the required accuracy. If the exponent 1/2 is used, and ω is not independent of T, then the experimentally determined value of b corresponds to an average value of ω over the temperature range of the measurements. It is possible, however, that the average value of ω so determined may differ appreciably from the average value of the true work function.

Apart from all differences arising from experimental error, real differences might be expected owing to the untenable nature of one or more of the assumptions involved in the derivation of Richardson's equation. The argument by which the equation is developed is essentially thermodynamic, yet the equations of thermodynamics have to do only with states of equilibrium, and in particular do not deal with such quantities as rates of emission. To arrive at the relation between rate of emission and temperature it is necessary to assume (1) that the laws of the kinetic theory of gases may be applied to an atmosphere of electrons in equilibrium with a thermionic source, (2) that the coefficient of reflection of electrons from the surface of such a source is zero, or at any rate, independent of temperature, and (3) that the rate of emission of electrons at a given temperature is as great when all emitted electrons are being drawn off as fast as liberated, as when the system is in equilibrium, or, at least, that there is a fixed ratio between these rates. The failure of any one of these conditions may lead to incorrect estimates of the thermionic work function calculated from the b constant of Richardson's equation, without necessarily affecting the appropriateness of the equation to represent the temperature-emission relation. Thus there is some theoretical importance attached to direct comparisons between calorimetrically determined work functions and corresponding values of the quantity, kb/e, obtained from temperature-emission data.

Calorimetric determinations of the work function may be made in the case of thermionic emission by measurements on what is generally referred to as the cooling effect. Such measurements were first attempted by Wehnelt and Jentzsch[1] working with lime coated filaments. The experimental conditions under which these investigators worked appear to have been too far from ideal, however, to permit of their obtaining any satisfactory results. The first successful measurements were made by Cooke and Richardson on osmium filaments[2] and later on tungsten filaments.[3] Other measurements have since been made for tungsten, carbon, molybdenum and tantalum by H. H. Lester.[4] The values of φ determined in these experiments have ranged from 4 to 6 volts, and are, therefore, in approximate agreement with the values of φ determined for these same materials from their values of b. In the case of tungsten Lester found that his value of φ determined by the cooling method agreed to within 0.7 of one per cent. with a value previously calculated by Langmuir from the value of b determined for a filament from the same batch of pure tungsten. While this agreement is well within the limits of experimental error there is some question as to how much importance should be attached to it. The thermionic properties of metals are appreciably altered by very slight gaseous or other contamination; and for this reason it is doubtful if a comparison based on different filaments, even though they be from the same batch of metal, can ever be regarded as satisfactory.

Direct comparisons of values of φ determined in the two ways were made in 1917 by Dr. Wilson[5] of this laboratory for the emission from various oxide coated filaments. While these experiments were not designed as a critical study of the thermionic work function as such, the values found for individual filaments by the two methods were in very good agreement.

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[1] Ann. d. Phys., 28, p. 537 (1909).

[2] Phil. Mag., 25, p. 624 (1913).

[3] Phil. Mag., 26, p. 472 (1913).

[4] Phil. Mag., 35, p. 197 (1916).

[5] Nat. Acad. Sci., Proc. 3, p. 426 (1917).

The purpose of this paper is to present results obtained by us in the measurement of the work function by the two methods simultaneously upon a single filament of pure tungsten. The calorimetric measurements are described in Part I., the temperature-emission measurements in Part II., and this is followed by a discussion of the results of the two sets of measurements.

Part I. Calorimetric Measurement of φ.

A. Theory of the Measurement.

The general scheme of the experimental arrangement used in these measurements is shown in the circuit diagram, Fig. 1. The filament to be tested, *FF*, is provided with potential leads at *pp*, far enough removed from the ends of the filament to avoid effects arising from end cooling, and means are provided (not indicated in the diagram) for limiting the emission of electrons from the filament to the region between these points.

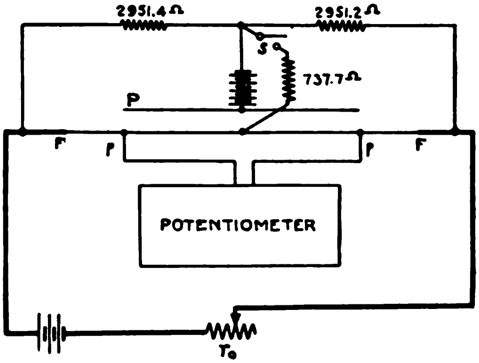

Fig. 1.

With the plate *P* at a negative potential and a heating current of *I* amperes through the filament the difference of potential between the points *p* is, say, *E* volts. We have then for the resistance of the filament, $R = E/I$ ohms, and for the net radiation, $W = EI$ watts. It is assumed that *R* and *W* are functions of temperature only, and in particular that they are independent of whether or not electrons are being drawn from the filament. This does not apply in general to the total power supplied to the filament but only to that portion of the total power which goes to maintain thermal radiation. *W* may then be regarded as a function of

R, and any small change in R is accompanied by a small change in W such that

$$\Delta W = \frac{dW}{dR}\Delta R = I^2 \frac{I\dfrac{dE}{dI} + E}{I\dfrac{dE}{dI} - E}\Delta R.$$

If now the plate P is switched to a positive potential an electron current of i amperes, which for the present will be supposed small compared to I, flows from the filament and simultaneously the heating current becomes $I + \Delta I$ and the voltage drop $E + \Delta E$.

We must now distinguish carefully between $\overline{W}$ the total power supplied to the filament and W the power radiated from it. Without space current these are equal. When the space current is switched on, however, they are altered in different amounts. The increase in $\overline{W}$ is given by

$$\Delta\overline{W} = I\Delta E + E\Delta I,$$

while the increase in W must be calculated from the change in resistance of the filament and the known rate of variation of W with R. Thus $\Delta R = (I\Delta E - E\Delta I)/I^2$ and

$$\Delta W = \left[\frac{I\dfrac{dE}{dI} + E}{I\dfrac{dE}{dI} - E}\right](I\Delta E - E\Delta I).$$

The difference between these two increments is the power absorbed by the thermionic emission. Expressing this as a voltage, φ, times the emission, i, we have,

$$\varphi i = \Delta\overline{W} - \Delta W = \left[\frac{2EI}{E - I\dfrac{dE}{dI}}\right]\left(\Delta E - \frac{dE}{dI}\Delta I\right).$$

In using this relation to determine φ it has been found convenient to compensate the change in filament resistance by an appropriate alteration in the resistance r_0, so that ΔI is made zero. φ is then calculated from the expression,

$$\varphi = \left[\frac{2EI}{E - I\dfrac{dE}{dI}}\right]\frac{\Delta E}{i} = Q\frac{\Delta E}{i}.$$

In order that this formula shall yield the true value of φ the value of ΔE employed must be the voltage change actually due to the cooling effect of the emission. In addition to this true ΔE, the existence of emission gives rise to several other voltage changes across the filament. A considerable share of the first part of this paper is taken up by a consideration of these spurious changes. Some of these reverse sign relative to the true effect with reversal of the heating current and are eliminated from the results by averaging observations made with the two directions of heating current. Others, however, do not reverse sign in this way.

One such effect that requires special attention results from the change in temperature of the plates under electron bombardment. A part of the additional radiation from the plates is absorbed by the filament giving rise to an increase in filament temperature and resistance, and in consequence to a change in voltage across the filament. Another cause of error arises from the dissymmetry of the potential field. The emission of electrons from the filament is limited to the portion between the potential leads by electrostatic guard boxes surrounding the ends of the filament and maintained a few volts negative to it. On account of the drop in potential along the filament the relations between plate, guard and filament potentials are not the same at the two ends of the filament. This gives rise to a slight shift of the center of emission toward the negative end and to a voltage change that is unrelated to the cooling. Both of these effects are important even when i is small in comparison with I.

If i is not small compared with I still another spurious voltage change becomes important. This results from the addition of the returned space current to the normal heating current with the consequent variation of total effective heating current from point to point along the filament. We shall begin by considering this last effect somewhat in detail.

The total potential drop across the filament is always

$$E = \int_{-\frac{1}{2}L}^{\frac{1}{2}L} \rho I dx,$$

where L is the total length of the filament (between potential leads) and ρ is the resistance per unit length. The variation of this integral is

$$\Delta E = \int_{-\frac{1}{2}L}^{\frac{1}{2}L} (\rho \delta I + I \delta \rho) dx.$$

If we disregard for the time the effect of cooling then $\rho = f(I)$, and

$$\delta \rho = \frac{d\rho}{dI} \delta I = \frac{d\rho}{dI} i,$$

where i now represents the space current flowing in the filament at the point x. Thus the change in voltage under consideration is given by

$$\Delta E' = \rho' \int_{-\frac{1}{2}L}^{\frac{1}{2}L} i dx,$$

where $\rho' = \rho + I(d\rho/dI)$.

To obtain an expression for i as a function of x we have the following relations:

$$\omega = \rho I^2 + I\left(2\rho + I\frac{d\rho}{dI}\right)i \text{ watts} \tag{1}$$

where ω is the power radiated per cm. of filament.

$$\omega = \pi d\epsilon\sigma T^4 = \pi d\epsilon_0\sigma T^5 \text{ watts,} \tag{2}$$

where d is the diameter of the filament in cm., σ is the Stefan-Boltzmann radiation constant, and $\epsilon = \epsilon_0 T$ is the total thermal emissive power of tungsten, which is closely proportional to T over the range of our measurements.

$$S = -\frac{di}{dx} = \pi dAT^{1/2}\epsilon^{-b/T}, \tag{3}$$

where S is the emission per cm. of filament, and A and b are the constants of Richardson's equation. Here and in what follows the positive direction of current is taken to coincide with the direction of flow of electrons, and the sign of potential gradient along the filament is also reversed.

Combining the above relations it can be shown that, to a close approximation, the value of i at the point x is

$$i = \frac{1}{\beta}\log\frac{1}{\beta S_0 x + C},$$

where S_0 is the emission per cm. of filament for heating current I

$$\beta = \frac{b\left(2\rho + I\dfrac{d\rho}{dI}\right)}{5\rho I}\left\{\frac{\pi d\epsilon_0\sigma}{\rho I^2}\right\}^{1/5}$$

and C is a constant of integration.

If the current flowing into the filament at the point $-\frac{1}{2}L$ is $(I + i_1)$ and that flowing out of the filament at the point $\frac{1}{2}L$ is $(I + i_2)$, then

$$i = i_0 - \frac{1}{\beta}\log\left(\cosh\beta i' + \frac{2x}{L}\sinh\beta i'\right),$$

where

$$i_0 = \frac{1}{2}(i_1 + i_2) \qquad \text{and} \qquad i' = \frac{1}{2}(i_1 - i_2).$$

Substituting this value of i into the expression for $\Delta E'$, and integrating, we find

$$\Delta E' = \rho' L\left[i_0 + \frac{1}{\beta}(1 - \beta i'\cosh\beta i')\right]$$

or to a close approximation

$$\Delta E' = \rho' L\left(i_0 - \frac{\beta}{3}i'^2\right).$$

If we now, as formerly, use i to represent the total emission from the filament, we have, for the case in which the space current is returned equally to the two ends of the filament, $i_1 = -i_2 = 1/2i$ so that $i_0 = 0$ and $i' = 1/2i$, and

$$\Delta E' = -\frac{\beta}{12}\rho' L i^2.$$

It is to be noted that the voltage change is, in this case, negative. It is of the same sign as the change due to the cooling effect, and results, if not allowed for, in too great a value of the work function.

If the space current instead of being returned to the ends of the filament, as in the case just considered, is returned to the middle point of the filament, conditions are considerably altered. In computing the spurious ΔE for this case the total effect is obtained by adding the effects computed for the two halves of the filament separately. In making this computation it must be borne in mind that when the space current is returned to the middle point of the filament it does not divide equally between the two halves, but that the greater part of it flows from the middle point in the direction of flow of the main heating current. When this dissymmetry is taken into account one finds for the total spurious voltage change in this case

$$\Delta E' = \frac{\beta}{24}\rho' L i^2.$$

The change is positive instead of negative and in magnitude it is one half as great as the $\Delta E'$ for the current returned equally to the ends of the filament. This suggests the possibility of so arranging the return of space current to the filament that the voltage change due to redistribution of the heating current is completely eliminated. It turns out from a deduction similar to those already indicated that to make $\Delta E'$ zero the current returned to the middle point must be four times as great as the current returned to each end. This condition is obtained in the circuit of Fig. 1 when the switch, S, is closed.

Measurements may also be made for the space current returned equally to the ends of the filament, and entirely to the middle of the filament. If the apparent values of the work function obtained in these ways are, respectively, φ_1 and φ_2, then the true work function is given by $\varphi = \frac{1}{3}(\varphi_1 + 2\varphi_2)$. This again avoids having to calculate the spurious ΔE.

Another source of error mentioned above is that due to the change in temperature of the filament that results from the heating of the plates under electron bombardment. When the space current is switched on the power, $w = Vi$, where V is the plate potential, is dissipated at the plates, and when the system has come to equilibrium the thermal radiation from the plates is increased by this amount. A fraction, f, of this radiation is absorbed by the filament, the value of f being determined by the geometry of the system and by the coefficient of absorption of the filament for the radiation reaching it. In calculating the error that this "back heating" introduces into the results we may disregard for the time the voltage changes due to all other causes.

When the space current is switched on the power radiated from the filament changes from $W = EI$ to $W + \Delta W = I(E + \Delta E'') + fw$, and the resistance of the filament changes from $R = E/I$ to $R + \Delta R = (E + \Delta E'')/I$, since I is kept constant.

From these relations we have

$$\frac{\Delta W}{\Delta R} = \frac{dW}{dR} = I^2 \left[\frac{I\dfrac{dE}{dI} + E}{I\dfrac{dE}{dI} - E} \right] = \frac{I\Delta E'' + fw}{\Delta E''/I}.$$

Solving this for $\Delta E''$

$$\Delta E'' = \frac{-fw}{\left[\dfrac{2EI}{E - I\dfrac{dE}{dI}} \right]} = \frac{-fVi}{Q}$$

or, since

$$\varphi = Q\frac{\Delta E}{i},$$

$$Q\frac{\Delta E''}{i} = \Delta\varphi = -fV,$$

i.e., the back heating causes an error in φ which is equal to $-f$ times the plate voltage. This relation is particularly interesting in showing that this error is independent of the magnitude of the space current.

The most satisfactory means we have found of correcting for this error is to observe the value of $\Delta E/i$ at constant filament current for a series of plate voltages, and then to extrapolate to the value of $\Delta E/i$ corresponding to plate voltage zero.

It seems advisable to omit consideration of effects arising from dissymmetry of the potential field, mentioned above, from this section as they can be dealt with more easily in connection with the experimental results.

As to the spurious voltage changes that reverse sign with reversal of the heating current, these result from geometrical dissymmetry and from variation in thermionic properties from point to point along the filament. It can be shown quite generally that all first order errors arising from these causes are eliminated from the results by averaging observations for the two directions of heating current.

B. Description of Tube and Circuit.

All satisfactory measurements were made upon a filament of very pure tungsten kindly supplied to us by Dr. Langmuir of the General Electric Company. The measured diameter of this filament was $(7.595 \pm .015) \times 10^{-3}$ cm. To it were welded at equal intervals three very fine tungsten leads of measured diameter 1.55×10^{-3} cm. These were to serve as potential leads and as space current return to the middle of the filament. The welding was performed under a microscope in an atmosphere of nitrogen. The fine leads were spaced as carefully as possible, and after welding the distances between leads were measured to be 3.849 ± .001 cm. and 3.842 ± .001 cm., respectively. At each point the fine filament was welded straight across the larger filament, so that there were really two leads attached at each of the three points.

The filament with fine leads attached was mounted as shown in Fig. 2. The lower end F_1, about 2.5 cm. from the potential lead P_1, was welded to a heavy platinum lead which passed directly through the press of the tube. The upper end of the filament F_2, about 2.5 cm. from the top potential lead P_2, was welded to a heavy platinum wire which in turn was supported from a glass arbor of the tube by a spiralled molybdenum spring. This heavy platinum wire passed through two small holes in a nickel guide, and in this way the tungsten filament was maintained straight and taut at all temperatures. The current lead to the top of the filament consisted of three flexible platinum ribbons welded to the heavy platinum wire below the nickel guide. These ribbons passed to a platinum lead-wire sealed through the top of the tube.

Heavy tungsten wires were welded to the fine tungsten potential leads about 1 cm. from the filament, and these in turn were welded to supporting wires and lead-in wires sealed through the bulb. The purpose of interposing tungsten wires adjacent to the potential leads was to avoid, as far as possible, the development of thermo-electric forces in the potentiometer circuit.

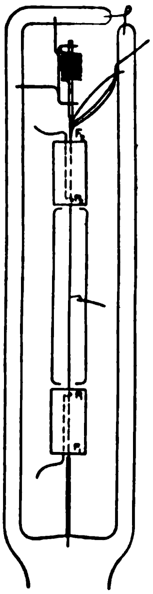

Fig. 2.

The space current leads to the middle of the filament, which were not to be used for potential leads, were fastened directly to nickel supports and finally led out through a platinum wire in the press.

The plates for receiving the space current and a pair of guard boxes for limiting the emission to the section of filament between the potential leads were made of molybdenum, and arranged as indicated in the figure. The plates were each 2.5 cm. by 7 cm., and bent inward slightly at top and bottom as shown. When mounted they were 1.25 cm. apart and symmetrically located with respect to the filament. The boxes were 2.5 cm. × 2.5 cm. × 1.25 cm., open toward the filament supports at the respective ends and closed at their opposite sides except for centrally located circular holes about 1 mm. in diameter through which the filament passed.

In order to free the parts from gas as much as possible, the glass parts were baked for several hours in a vacuum furnace at about 500° C. before assembling, and all of the metal parts, with the exception of the molybdenum spring and the tungsten filaments, were pre-glowed in vacuo at a high temperature. On the pumps the main tube and a Buckley ionization manometer which was sealed to it were baked out at 400° C. The molybdenum plates were raised to white heat by electron bombardment from auxiliary tungsten filaments mounted outside the plates, and the guard boxes were heated to about 1500° C. by Foucault currents induced from a high frequency current in a solenoid surrounding the tube. The procedure of alternately baking the tube and heating the metal parts, as described, was repeated several times. The tube was finally sealed from the pumps at a pressure of about 1×10^{-6} mm. Hg with the molybdenum plates at a white heat.

None of the final measurements were made until the tube had been in circuit over a month. During all this time some of the filaments were heated and for a large part of it all the filaments were hot and furnishing space currents. The final pressure obtained with the main filament cold was below 5×10^{-8} mm. Hg and was scarcely measurable. With the main filament at its highest temperature the pressure was about 5×10^{-7} mm. Hg.

Throughout these final measurements the main filament and one of the two manometer filaments, which were of tungsten, were glowed continuously. The main filament was cold for only a few minutes about twice a week while the storage batteries were being changed. This precaution was found necessary to insure extreme steadiness of emission. By taking this precaution measurements made at any working temperature under identical conditions seldom differed by as much as 2 per cent.

after an interval of several weeks. Under the ordinary working conditions unsteadiness of emission was never a disturbing factor.

All the essential measurements were made with a Leeds and Northrup potentiometer. As the maximum potential between the potential leads was about 12 volts the potentiometer could not be used in the normal way. In place of the customary 2-volt storage cell a battery of 18 volts was used across the potentiometer and the current adjusted to balance a Weston Standard Cell across a single 5-ohm coil. With this arrangement the potentiometer readings could be reduced to volts by multiplying by the factor 10.1870, and the maximum range of the instrument was about 16.3 volts instead of the usual 1.60 volts.

The accuracy of the potentiometer was checked by comparing together four coils taken at random and by comparing a coil with the slide wire. The coils were found to be identical but the slide-wire had a slightly low resistance. A reading on the slide-wire could be reduced to a "coil reading" by dividing by 1.0014(5). This ratio was checked for several different points on the slide-wire, and it was found to hold when the potentiometer was balanced in the normal way as well as when it was balanced with the standard cell across one coil. Correction for this ratio was made before using any reading taken on the potentiometer.

The voltage between the potential leads was measured directly on the potentiometer. The potentiometer was also used in determining the heating current and the space current from the filament, in the first case from measurements of the voltage across a standard ohm in series with the filament, and in the second from the voltage across a variable resistance dial box through which the space current flowed. The steps of this dial box were measured and found to be sufficiently accurate. The certificate of Leeds and Northrup gave the resistance of the standard ohm as .99997 International ohms at 25° C. No correction was made for its resistance not being exactly one ohm.

The arrangement just indicated suffices for taking the points of the $E - I$ curve and from them determining the function,

$$Q = \frac{2EI}{E - I\dfrac{dE}{dI}},$$

for the different values of I at which the cooling is to be measured. It is also satisfactory for measuring the emission as a function of I. The temperatures can be found from the $E - I$ curve together with the known temperature characteristics of tungsten and thus all the data are available for finding the constants of Richardson's equation.

The measurement of ΔE, which is the essential datum in determining φ, cannot be satisfactorily carried out with the arrangement described. The actual magnitude of ΔE for our filament was always in the neighborhood of 2 volts per ampere of space current. Thus, in order to measure ΔE correct to 1 per cent. for an emission of 1×10^{-3} amperes, it would be necessary to determine the voltage change represented by ΔE correct to 2×10^{-5} volts, or approximately 1/50 of a division on the slide-wire; the total ΔE would correspond to only 2 divisions. Since dE/dI for the filament was about 20 volts per ampere, an error of 1/10 of one division in the resetting of I would involve an error of 100 per cent. in ΔE. Also slow time changes in the filament heating current and the potentiometer current always occurred, and it was thus necessary to measure E very quickly indeed after setting these currents to their correct values.

The necessary accuracy in resetting the filament current was finally obtained by placing in series with the filament a fixed resistance of such magnitude that the desired heating current was established by making the voltage across this resistance equal to that of the standard cell. (An appropriate series of heating currents was obtained by using an appropriate series of such fixed resistances.) By this procedure the accuracy of resetting the heating current is not made to depend upon the accuracy of resetting the potentiometer. Great care was taken for maintaining the heating current and the potentiometer current steady, and rapid manipulation was aided by a convenient arrangement of switches and regulating resistances.

After these factors had been satisfactorily taken care of, it became feasible to increase the sensitivity of the potentiometer for directly reading the change in E. This was accomplished by applying the 18-volt potentiometer battery across the potentiometer in series with two variable external resistances (a and b in Fig. 3). The standard cell was balanced against the potentiometer in the normal way, the bulk of the 18 volts being taken up across these resistances. The circuit was arranged to balance the voltage between the filament potential leads across one of the external resistances and part of the slide-wire. With this arrangement the values of these resistances were not required as only changes in E were measured and these changes fell well within the limits of the slide wire. The potentiometer sensitivity is now normal.

With these improvements in the circuit ΔE could be determined with a satisfactory accuracy for as low a space current as 0.6×10^{-3} amperes. The practical upper limit to the emission was about 9.5×10^{-3} amperes. It was planned to determine ΔE, and thus φ, for eight different filament temperatures including the temperatures which gave these two extreme values to the emission. For this purpose it was necessary to have the fixed resistance in the filament circuit adjustable to eight values which would determine these required temperatures. This resistance was made of a length of No. 17 "Ideal" resistance wire wound upon a copper tube. It was divided into four sections, three of which could be shunted by heavy amalgamated copper bars dipping into cups of mercury. By different combinations of these shunts eight different fixed resistances were available. These resistance steps were very constant, no variation in any of them as great as .005 per cent. being found during a period of fourteen months.

The essential features of the circuit have already been described. For the sake of completeness a simplified diagram of the circuit showing the more important switches is given in Fig. 3. The arrangement for returning the space current to the filament in the three different ways is not shown, nor are the means for using the 18 volts straight across the potentiometer and balancing the standard cell across one coil. The electrostatic shields which limit the emission from the filament are not

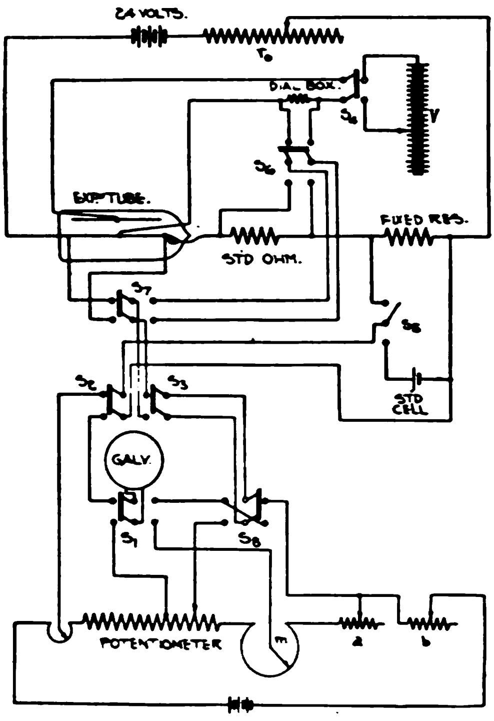

Fig. 3.

shown. Means were provided for varying the potentials of these two shields independently. The space voltage, V, could be varied in steps of one dry cell from one cell to a voltage of 500, and it could be applied in either direction between the filament and plate. A reversing switch was inserted in the filament circuit so that observations could be made for both directions of heating current. This necessitated reversing switches for the potentiometer current, for the galvanometer, for the standard cell, and for the potential leads from the space current dial box. These five reversing switches were arranged to be operated simultaneously. There were other switches for increasing the convenience and accuracy of measurements, but these need not be considered here.

It may be instructive to trace the manipulation of switches in a typical measurement of $\Delta E/i$. At the beginning S_1 is left, S_4 open, S_5 down, S_6 up, S_7 left, and S_8 right. S_2 is closed and b adjusted to balance the potentiometer against the standard cell. Next S_5 is thrown up and r_0 adjusted to a balance. Then S_1 is thrown to the right and at the same time S_3 closed (opening S_2, these switches being mechanically interlocked so that both cannot be closed at one time), and the slide wire, m, is adjusted to a balance—reading E between the potential leads. The switches are then returned to their original positions, S_4 is closed and the same thing repeated. The change in the slide wire reading gives ΔE for constant filament heating current. S_8 is thrown to the left and S_7 to the right, and the potentiometer balance gives the voltage across the dial box and thus the value of i. In carrying out these measurements each slide-wire setting could be checked carefully in about two or three seconds when the conditions were satisfactory. Readings were taken against time before closing S_4 and again after closing S_4. Lines were passed through the resulting points and the interval between these lines used as ΔE.

C. *Experimental Results.*

The calorimetric measurement of φ requires the determination of the function

$$Q = \frac{2EI}{E - I\dfrac{dE}{dI}}$$

and of $\Delta E/i$. This latter involves the careful evaluation of the corrections to be applied to ΔE. Thus there are three sections of the work which will be taken up in order.

(Determination of Q.)

The only difficulty in connection with the determination of values of Q is in obtaining sufficiently accurate values of the differential coefficient

dE/dI. The procedure adopted was first to set up an empirical equation for E by evaluating the coefficients of the power series $E = A_0 + A_1I + A_2I^2 + A_3I^3 + A_4I^4$ and then to calculate dE/dI for the eight points from $dE/dI = A_1 + 2A_2I + 3A_3I^2 + 4A_4I^3$. The labor involved in evaluating the coefficients in the equation for E was materially reduced by using pairs of values of E and I corresponding to equal intervals in I, and applying a method recently described by T. C. Tobin.[1]

The results of these measurements and calculations are collected in Table I. A considerably greater number of pairs of values of E and I was taken than was actually required for the determination of values of Q. These were for use in connection with the temperature-emission measurements to be described later. The pairs of values designated as "exact" in column 4 are those used in evaluating the power series for E. The computed values of E in the same column agree with the observed values in column 3 almost within the limit of error of the measurements. The values of Q cannot be in error by more than a few parts in 10,000.

TABLE I.

$I \Big/ \frac{10.1870}{1.00145}$.	I (amp.).	E (volts).	E (Computed from Empirical Equation).	$\frac{dE}{dI}$ (volts/amp.).	Q (amp.).	Q (Filament) (Shunted).
.052	.52895	4.6757				
.055	.55947	5.1189				
.058	.58999	5.5821				
.061	.62050	6.0604	6.0604			
.064	.65102	6.5582	Exact			
.067	.68154	7.0715	7.0723			
Fixed res. No. 1	.70646	7.5026	—	17.580	2.1558	2.1508
.070	.71205	7.6033	Exact			
Fixed res. No. 2	.72182	7.7777	—	17.869	2.1927	2.1874
Fixed res. No. 3	.74054	8.1140	—	18.224	2.2330	2.2280
.073	.74257	8.1517	8.1518			
Fixed res. No. 4	.75773	8.4306	—	18.552	2.2707	2.2654
.076	.77309	8.7180	Exact			
Fixed res. No. 5	.78692	8.9802	—	19.106	2.3344	2.3287
.079	.80360	9.3023	9.3019			
Fixed res. No. 6	.80615	9.3520	—	19.467	2.3779	2.3718
Fixed res. No. 7	.82975	9.8157	—	19.901	2.4323	2.4258
.082	.83412	9.9220	Exact			
Fixed res. No. 8	.85151	10.2516	—	20.290	2.4852	2.4780
.085	.86464	10.5200	10.5211			
.088	.89515	11.1559	Exact			
.091	.92567	11.8088	—			

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[1] Phil. Mag., 40, p. 513 (1920).

It should be noted that the above values of E refer to the filament when not shunted by the high-resistance bridge used for returning the space current to the filament ends, as in Fig. 1. When so shunted the current flowing through the filament is less than that measured on the potentiometer by the amount of the bridge current. The last column of Table I. gives the values of Q corresponding to the eight fixed resistance points with the filament shunted in this way. These are the values to be used in the case of space current returned to the ends of the filament or to the middle and ends.

The factor Q has the dimensions of current and is, therefore, independent of the length of the filament. When space current is flowing the heating current and also Q varies from point to point along the filament. Thus it is not strictly accurate to regard Q as a constant depending only on I. It can be shown, however, that for the case in which the space current is returned equally to the two ends of the filament, this variation is taken care of by multiplying the apparent value of φ by the factor

$$\left[1 - \frac{1}{12}\left(\frac{i}{Q}\frac{dQ}{dI}\right)^2\right].$$

Evaluating this by means of data from Tables I. and IV. it is found to differ from unity at most by only one part in 10^6.

(Determination of $\Delta E/i$.)

For all measurements in which space current is drawn from the filament it is necessary that the plate voltage be high enough to cause saturation of the emission over the main length of the filament and up to points near the ends where it is cut off fairly sharply by the boxes which shield the ends. It is impossible, of course, that the emission should be in voltage saturation quite up to the points of complete cutoff. An approximate approach to this condition is, however, possible by using a sufficiently high plate voltage. On the other hand, the correction to ΔE due to the back heating from the plates is proportional to the plate voltage and, therefore, this voltage should be as low as possible. From observations to be described later an effective plate potential of 196 volts, measured from the filament mid-point, was chosen as a satisfactory value. This effective voltage is the value read on the voltmeter decreased by the fall of potential caused by the space current flowing through the high-resistance bridge.

The procedure of measuring $\Delta E/i$ has been indicated in section B. Typical data giving one such measurement are shown in Table II.

Table II.

Measurement of $\Delta E/i$.

Fixed Res. Point No. 7—*i* Returned to Middle of Filament—Direction of Filament Current (1).

Time (Mins.).	Slide Wire Reading of E.	V (Volts).	Time. (Mins.).	Slide Wire Reading of E.	V (Volts).
0	.02696	Off	14	.04088	—
1	705	Off	14½	082	—
2	705	Off	15		Off
3½	691	Off	17	.02673	Off
4	695	Off	18	672	Off
4		On	19½	675	Off
6	.04095	204	20	672	Off
7	105	—	22½	690	Off
7½	096	—	23	686	Off
9½[1]		—	24	691	Off
11	094	—	25	692	Off
12½	079	—	26	690	Off
13	084	—			

By plotting carefully against time the values of the slide-wire reading of E we determine,

$$\Delta E = -\ .00287(0) \text{ volts.}$$
$$\text{Dial Box Res.} = 100.0 \text{ ohms;}$$
$$\therefore i = .006660 \text{ amp.}$$
$$\Delta E/i = -\ 2.081 \text{ volts/amp.}$$
$$\text{Effective } V = 196 \text{ volts.}$$

At each of the eight fixed resistance points determinations of $\Delta E/i$ were made in this way for the space current returned to the middle of the filament, to the ends of the filament, and to the middle and ends. These measurements were made for the two directions of heating current through the filament, a total of forty-eight determinations of $\Delta E/i$. The results of this series of measurements at one typical point are shown in Table III. The product of $\Delta E/i$ with the corresponding value of Q is designated as φ'. In order to save space the results are not completely tabulated here.

Table III.

Fixed Res.	Direction of Filament Current.	Space Current Return.	$i \times 10^3$ (amp.).	$\frac{\Delta E}{i}$ (volts/amp.).	φ' (volts).	Mean φ' for 2 Directions of Fil. Current.
No. 7	1.......	Middle....	6.660	2.081	5.065	4.635
		Ends......	6.351	2.222	5.395	5.207
		M. and E. .	6.338	2.095	5.085	4.797
	2.......	Middle....	6.697	1.728	4.205	
		Ends......	6.377	2.070	5.02	
		M. and E. .	6.390	1.858	4.51	

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[1] Pot. Reading on Dial Box, .66606.

It will be noted that the values of φ' for direction of heating current (1) are higher than for direction (2). (Throughout all the measurements the difference was uniformly about 14 per cent.) This failure of values to check on reversal results, as already mentioned, from geometrical dissymmetry. In the present case the failure was found to result from a slight difference in average diameter between the two halves of the filament, and from a dissymmetry in the location of the guard boxes. The effect to be expected from these departures from symmetry has been carefully estimated and found sufficient to account for the observed dependence of $\Delta E/i$ upon the direction of heating current. The mean values of φ' for the two directions are correct, so far as these effects are concerned, to the second order of small quantities.

These mean values of φ' are plotted against i in Fig. 4. The points marked + are placed 1/3 the distance from the ⊙ points to the × points. Note that these coincide almost perfectly with the ⊕ points as required by theory,—except for values of i below 1 mil where ΔE is very small and the experimental errors in determining the values of φ' are large. Taking 4.81 to be the true mean value of φ', the temperature shift formulæ of section A lead to the curves represented by the dotted lines. These are in reasonably good agreement with the observed points. We are thus justified in concluding that the temperature shift effect is eliminated from the values of φ' for the space current returned to the middle and ends.

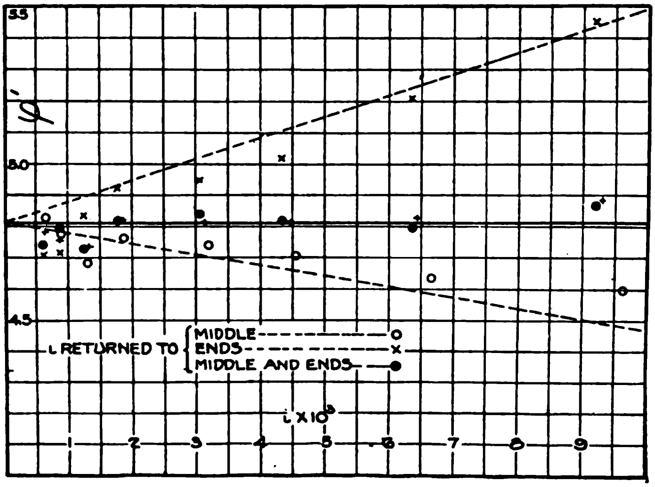

Fig. 4.

(Corrections to φ'.)

In Fig. 5 the mean values of φ' of Fig. 4 are replotted against abscissæ representing absolute temperatures. (The determination of these temperatures is taken up in Part II.) Only the ⊕ points and the + points are shown in Fig. 5. Each point, if it were corrected for the back heating from the plates and for the effect of the electrostatic shields, would represent an experimental measurement of φ itself. The actual method employed in the final evaluation of φ consisted of a careful determination of these two errors at the fixed resistance point No. 7, and an application of the results to the best value of φ' obtained by smoothing the points of Fig. 5.

The solid line in Fig. 5 is drawn for φ' = constant and the dotted line represents

$$\varphi' = \varphi_0' + \frac{3}{2}\frac{kT}{e},$$

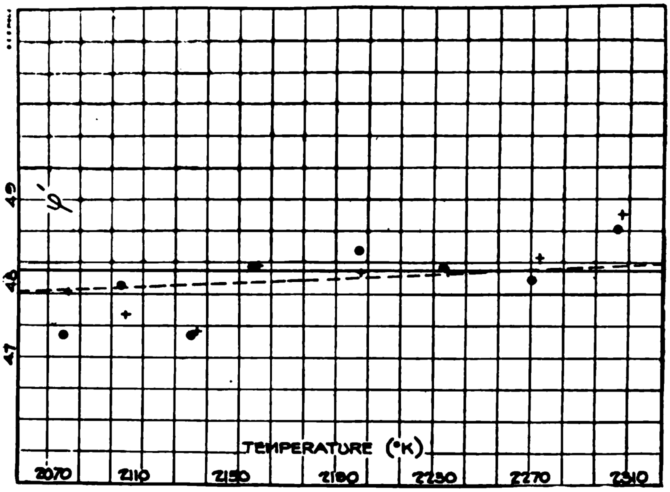

Fig. 5.

corresponding respectively to the first and second forms of Richardson's equation. Neither of these lines seems to fit the points as well as they can be fitted. The best line would have a slope about twice that of the dotted line, *i.e.*, about $3k/e$. It is possible, however, that this greater variation is more apparent than real. Reasons are given in another section for thinking that the value found for φ' at 2306° K. is higher than the true value for this temperature, while the values found at the lowest temperatures are subject to considerable error on account of the smallness of the emission. On the other hand, it does not seem impossible to modify the thermodynamic requirements in this connection by modifying somewhat our view in regard to the nature of the system. We hope to consider this possibility more fully in a paper now in preparation on the work function of oxide-coated filament.

Whatever the variation of the work function with temperature, Fig. 5 determines the value of φ' at the fixed resistance point No. 7 to be 4.81 volts, which is probably correct to ± .015 volt. This is the final value of φ'. Correction must be made for the effect of the electrostatic shields and for the back heating from the plates before the true value of φ is obtained.

The error due to the electrostatic shields results from the fact that if the two shields are maintained at the same negative potential relative to the middle point of the filament, as was the case in the measurements so far described, the "grid action" at the positive end of the filament is more marked than at the negative end. This has the effect of shifting the center of emission toward the negative end of the filament and of introducing an error in ΔE which does not reverse sign relative to the true effect on reversal of the heating current. It is possible to avoid this error by maintaining the same difference of potential between shield and adjacent portion of filament at each end. The importance of this correction was not appreciated, however, until observations were nearly completed, and the shields were maintained throughout at -11.57 volts relative to the middle point of the filament.

It can be shown that if the center of emission shifts a distance δ when the heating current is reversed a spurious voltage change is introduced which is given by

$$\Delta E'' = -\frac{i\delta}{2L}\frac{dE}{dI},$$

regardless of the way in which the space current is returned to the filament. This results, if not corrected for, in a value of φ' which is in error by being too large.

The magnitude of δ for the seventh point has been calculated from the change in emission which occurs when the potential of the shield at the positive end of the filament is increased from its normal value by an amount equal to the potential drop along the filament between the shields. This makes the potential difference between filament and shield the same at the two ends, and causes an increase in current corresponding to $\delta = .0335$ cm. for one direction of heating current and to $\delta = .0352$ cm. for the other. The difference of about 5 per cent. between these values probably arises from a slight geometrical difference between the situations of the boxes about the filament. The mean of these corresponds to a correction to φ' of -2.24 per cent.

To check this calculated correction, values of φ' were redetermined for the two directions of heating current, maintaining the proper relations between filament and box potentials. Successive measurements gave values lower than the former values by respectively 1.50 per cent. and 2.01 per cent. for one direction of heating current and 2.52 per cent. and 1.74 per cent. for the other direction. These are in agreement with the computed amount of the correction, although the accuracy of the direct measurements is not sufficiently good to afford a close quantitative check.

The original value of φ' corrected by $-$ 2.24 per cent. gives 4.702 volts, and this we regard as more reliable than the redetermined values. There remains only the correction due to radiation from the plates.

The method of determining the correction due to the heating of the plates has been indicated in section A. It consists in plotting $\Delta E/i$ against plate voltage for constant heating current with i returned to the middle and ends. This was carried out at the 7th point of the fixed resistance, for direction No. 1 of the heating current and with the boxes maintained in the correct potential relations to the main filament. The procedure adopted in these measurements was to determine

$$\delta\left(\frac{\Delta E}{i}\right) = \frac{i\delta\Delta E - \Delta E\delta i}{i^2}$$

for changes in plate potential from the standard value, 196 volts, to other potentials above and below this value. The data were then used to evaluate the ratio

$$\delta\left(\frac{\Delta E}{i}\right)\Big/\left(\frac{\Delta E}{i}\right)_{196}.$$

The results of these measurements are shown graphically by the points in Fig. 6. It will be noted that from V = 140 volts to V = 350

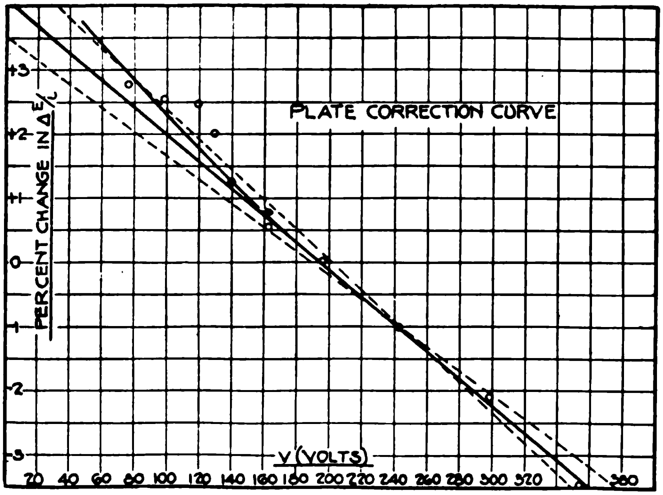

Fig. 6.

volts the variation in $\Delta E/i$ is sensibly linear. The best line through these points has a slope -0.0210 per cent. per volt, so that the apparent value of φ for $V = 196$ volts must be increased by $196 \times 0.0210 = 4.12$ per cent., this fraction applying not to the above corrected value of φ' but to the value which would be actually measured under the conditions of the test. This value is 5.036 volts, and thus the value of φ for the seventh point is increased from 4.702 volts to the final value 4.91 volts. The estimated possible errors in this plate correction determination are represented in the figure by the two dotted lines.

In establishing lines in Fig. 6 the points for V less than 140 volts have been disregarded because of another voltage dissymmetry which gives rise to spurious effects when the plate potential is sufficiently low. At each end of the filament the emission is cut off more or less sharply near the point at which the filament enters the guard box. The position of this cut off depends not only upon the difference of potential between box and filament, but also upon that between plate and filament and upon the density of emission. If the plate potential is sufficiently high the fact that the difference between plate and filament is greater at one end than at the other is unimportant. As the plate potential is reduced, however, this dissymmetry becomes more marked and results in an appreciable shift of the center of emission toward the negative end of the filament, causing a spurious increase in $\Delta E/i$. It was from preliminary measurements of the plate correction at the seventh point that 196 volts was chosen as sufficiently high to make the effect of this shift negligible. We believe the measured values of φ' at the eighth point are high (see Figs. 4 and 5) because this voltage was too low for the density of emission from the filament at this point.

As a check on the plate correction we may calculate roughly what correction is to be expected. It was shown in another section that the correction to φ is given by $-fV$, where f is the fraction of the power dissipated at the plates that is absorbed by the filament. The diameter of the filament is .00755 cm. and its distance from the plates 0.63 cm. If we assume that the power is dissipated along the normal projections of the filament on the plates and that the radiation proceeds from these lines, equally from the two sides of each plate and in accordance with the cosine law, then the fraction .003 of the total radiation is intercepted by the filament. If the coefficient of absorption of the filament for this radiation is λ, then $f = .003\lambda = \Delta\varphi/V$. From the measurements $\Delta\varphi/V = 0.04\varphi/196$. Taking φ as 5 we find $\lambda = 0.35$ which is a reasonable value for this constant. We conclude, therefore, that the experimental estimate of the plate correction is about what might be expected.

We have thus applied two corrections to the original apparent value 4.81 volts and have arrived at 4.91 volts as the final correct value of φ at the seventh point. The temperature for this point is 2270° K.

The possible absolute errors in determining, first, the apparent value of φ, second, the voltage-shift correction, and third, the plate correction are estimated to be ± .015 volt, ± .005 volt, and ± .025 volt. The most unfavorable cumulative error we thus estimate as ± 0.045 volt or about one per cent. of the value of φ.

Part II. Measurement of "b" in Richardson's Equation.

The more common form of Richardson's equation is

$$i = AT^{1/2}\epsilon^{-b/T}.$$

The constants of this equation, A and b, can be readily determined and the adequacy of the equation tested by plotting ($\log i - \frac{1}{2}\log T$) against $1/T$. This should give a straight line having the slope $- b \log \epsilon$. From the value of b obtained in this way, φ, the equivalent voltage of the work function, is determined from the relation, $\varphi = bk/e$. It is the purpose of this part of the paper to describe the determination of φ in this way, and to compare the value with that obtained by the direct calorimetric measurement.

With the potentiometer arrangement described in Part I. the relation between the emission from our filament, i, and the heating current, I, was readily determined with great accuracy. Emission measurements were made over as wide a temperature range as possible, with the effective plate potential held at 196 volts. Both of the limits of this range were probably determined by gas in the tube, the emission being extremely steady except at very low and very high temperatures. For high temperatures the power dissipated upon the plates liberated sufficient gas from them to seriously change the emission. At very low filament temperatures gas was probably absorbed by the filament, resulting in a decrease in the emission.

Over the range from 0.1 to 10 milliamperes the emission was always extremely steady and data were taken only for this range. With the effective plate potential maintained constant, as well as the filament heating current, there was no certain difference in emission for the three methods of returning i to the filament. Also there was no change of i on reversal of the heating current. The emission data, upon which the determinations of b are based, are given in columns (1) and (2) of Table IV. The starred values of I correspond to the eight fixed resistance points used in the calorimetric determination. *It is of importance to* *note that the emission data were taken in the midst of the ΔE determinations, and that the condition of the filament was the same during these two sets of measurements.*

TABLE IV.

I (amp.).	$i \times 10^3$ (amp.).	Temperature (° K.).		I (amp.).	$i \times 10^3$ (amp.).	Temperature (° K.).	
		Langmuir.	W. and F.			Langmuir.	W. and F.
.52895		1772	1779	.75773*	1.902	2138	2158.0
.55947		1823	1833	.77309	2.538	2162	2182.0
.58999		1874	1884	.78692*	3.269	2183	2204.0
.62050	.09341	1923	1935.5	.80360	4.405	2207	2231.0
.65102	.1973	1973	1986.5	.80615*	4.606	2212	2235.0
.68154	.3967	2021	2036.0	.82975*	6.875	2247	2271.5
.70646*	.6784	2060	2077.5	.83412	7.394	2254	2280.0
.71205	.7656	2069	2086.5	.85151*	9.792	2279	2306.0
.72182*	.9363	2084	2102.0	.86464		2298	2327
.74054*	1.362	2113	2131.5	.89515		2342	2375
.74257	1.419	2116	2134.5	.92567		2386	2420

The accuracy of the measurement of b depends entirely upon the determination of temperature as a function of I. The temperatures were found from data for tungsten published by Langmuir,[1] and by Worthing and Forsythe,[2] using our measured values of E and I and the diameter and length of the filament.

The temperature of a filament is uniquely determined by its resistivity, $\pi d^2E/4lI$, or by the power radiated per unit area, $EI/\pi dl$. Here d is the diameter of the filament and l its length. For the sake of simplicity Langmuir used the functions, d^2E/lI and EI/dl. The temperature is, of course, also completely determined by the function resulting from any combination of these two functions. By eliminating successively each of the variables, I, d and l, we can obtain the three other "temperature functions," $(E\sqrt{d})/l$; $(E\sqrt[3]{I})/l$; $I/d^{3/2}$. Langmuir published values of these five functions for tungsten at temperatures from 300° K. to 3540° K., at steps of 100°. We plotted these tabulated values carefully on accurate cross-section paper. For each value of I in Table IV. the temperature was found in five ways by locating the directly measured temperature functions upon these curves.

The data of Worthing and Forsythe are contained in the two empirical equations,

$$\log_{10}\left(\frac{EI}{\pi dl}\right) = 3.680\,(\log_{10} T - 3.3) - \frac{1040}{T} + 1.900$$

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[1] PHYSICAL REVIEW, 7, p. 315 (1916).

[2] PHYSICAL REVIEW, 18, p. 144 (1921).

$$\frac{\pi d^2 E}{4lI} = 59.2 \times 10^{-6} \times \left(\frac{T}{2000}\right)^{1.200}.$$

In the second of these equations 59.2×10^{-6} represents the resistivity of tungsten at 2000° K. From these equations the five temperature functions given above were computed at steps of 25° over the range covered by the emission data. From the resulting curves five different determinations of temperature were obtained for each value of I, in exactly the same way as from the curves of Langmuir's figures. Temperatures could be read to within nearly 1° from Langmuir's curves and to within 0.5° from the curves of Worthing and Forsythe.

The temperatures actually determined from the five temperature functions differed considerably at each value of the heating current, for both the scale of Langmuir and the scale of Worthing and Forsythe. The only possible explanations of this discrepancy are, either, (1) our filament differs from the samples of tungsten forming the bases of the temperature scales; or (2) our measured values of the temperature functions are incorrect.

If this latter is the true explanation it can be easily shown that the error is entirely confined to our value of d. E and I are known with extreme accuracy and l with fair accuracy, while the measured diameter, 7.595×10^{-3} cm., is less accurate, and it is probable that this value was somewhat decreased by vaporization during pumping.

In examining for such a possible error temperatures were computed, at a given value of the heating current, for a number of assumed values of d. Plotting computed temperatures against d the curves corresponding to the different temperature functions intersect at a value about 0.5 per cent. lower than the measured diameter. Curves of this kind, based upon the scale of Worthing and Forsythe, were plotted for four different heating currents, including the two extreme values of the $E - I$ curve. At each heating current the curves intersected at the same value of d to well within the limit of experimental error in determining the curves. The actually measured points of intersection were as follows:

I (amp.)	.52895	.68154	.80360	.92568
d at intersection (cm. $\times 10^3$)	7.550	7.554	7.556	7.553

Using the mean value $d = 7.553 \times 10^{-3}$ cm., all of the five temperature functions determine the same temperature to within 1° at each of the twenty-two points of the $E - I$ curves. This is a temperature range of 641° K.

The fact that values of d determined for different values of I differ at most by one part in 1000 is an indication that the tungsten of our filament is the same as that for which Worthing and Forsythe's equations have been written. It is not, however, a proof of such identity since the constants of these equations can be altered somewhat and an equally good series of values of d obtained. This point has been carefully examined in connection with the variations in the constants from one sample of pure tungsten to another as reported in connection with the equations. As a result of this examination we believe that the temperatures which have been associated with the heating currents do not differ from Worthing and Forsythe's scale by more than two or three degrees. As regards true temperatures we carry over, of course, whatever differences there may be between Worthing and Forsythe's scale and the thermodynamic scale.

Temperature determinations from Langmuir's figures were not so consistent. For heating currents over most of the $E - I$ curve this scale yielded values of the diameter in the range 7.550 to 7.555×10^{-3} cm., in exact agreement with the other determinations. For low currents, however, a smaller value of the diameter was determined, the lowest point of the $E - I$ curve giving $d = 7.51 \times 10^{-3}$ cm. The best temperature determinations it was possible to obtain from Langmuir's data are based on the function, $(E\sqrt[3]{I})/l$. Taking $d = 7.55(3) \times 10^{-3}$ cm., these temperatures are in good agreement with the determinations from the other functions except for quite low values of I. At the lowest point of the $E - I$ curve the greatest difference is 14° K.

The temperature scale of Worthing and Forsythe is probably more accurate than that of Langmuir. Furthermore, our measurements do not give consistent results on the latter scale. Consequently the series of temperatures found from the scale of Worthing and Forsythe should be given much more weight than the temperatures from Langmuir's scale. These sets of values are given in columns (4) and (5) of Table IV.

The value of "b" was obtained in the ordinary way by plotting $(\log_{10} i - \frac{1}{2} \log_{10} T)$ against $(1/T)$. For the highest points the temperatures have been corrected by the computed temperature change arising from the cooling, the greatest correction amounting to $- 3.1$ degrees. The plotting was done with care on large cross-section paper. The points fall upon two straight lines, corresponding to the two sets of temperatures, with an accuracy considerably greater than could be shown in a figure here. No one of the points on the basis of Worthing and Forsythe's scale is more than one degree from its line. The maximum departure for the points based on Langmuir's scale is 2.3°.

The slopes of these two lines divided by $- \log_{10} \epsilon$ give the following values of b:

	b (degrees K.).	φ (volts).
Scale of W. and F.	5.541×10^4	4.778
Scale of Langmuir	5.646×10^4	4.869

In calculating corresponding values of φ we have used $k = 1.372 \times 10^{-16}$ ergs per degree and $e = 4.774 \times 10^{-10}$ e.s.u.

Of the two values of φ every consideration requires that we put greater reliance in the former. Some idea as to the probable error of this value may be gained from the consideration that, if the temperature at the lowest point is correct and the value of φ is one per cent. in error, then the temperature at the highest point must be in error by 4.3 degrees. On the other hand a uniform error of 10 degrees from one end of the range to the other produces only a one per cent. change in φ. It seems unlikely, then, that this value of φ should be in error by much over one per cent.

Discussion of Results.

The value found for φ by the calorimetric method, 4.91 volts, is 2.7 per cent. greater than the value, 4.778 volts, found for the same constant from temperature-emission data on the basis of Richardson's equation. We believe that this difference is greater than can be reasonably accounted for by experimental error. It was pointed out in the introduction that a difference between these values might exist because of the impossibility of properly inferring the pressure of electrons in equilibrium with a metal from the rate of emission of electrons from it. If this is the cause of the difference, the calorimetric value is to be regarded as the true value, and that determined from the temperature-emission relation as an apparent value only. Before accepting this explanation as likely it will be well to consider again just what the quantities are that are being compared.

In previous measurements of the calorimetric φ by the Wheatstone bridge method it has been customary to subtract from the total energy absorbed per electron the quantity $2k(T - T_0)$. This has been done on the assumption that electrons entering the bridge arm at temperature T_0 absorb this quantity of energy, on the average, before leaving the filament at temperature T. This term is $2k(T - T_0)$ rather than $3/2k(T - T_0)$ because we are dealing with electrons passing through surfaces rather than electrons contained in given volumes. On this basis our calorimetric value of φ requires no such correction since all measurements have been made on a filament of uniform temperature. The energy absorbed per electron measures directly the work done against electrical forces.

To be consistent with this view in regard to the calorimetric φ, we must suppose that the φ in Richardson's equation is also the equivalent voltage of work done against electrical forces only. Richardson has shown by means of a thermodynamic argument that, in general, φ must vary with temperature, and that to a close approximation it will depend upon temperature through the relation

$$\varphi = \varphi_0 + \frac{3}{2}\frac{k}{e}T,$$

where φ_0 is a constant. The approximation is in the coefficient of T which will differ slightly from $(3/2)(k/e)$ by an amount which depends for a particular metal upon the coefficient of its Thomson effect. If we disregard the approximate nature of this relation the general equation

$$i = AT^{1/2}\epsilon^{\int^{T}\frac{\varphi e}{kT^2}dT}$$

reduces to

$$i = AT^2\epsilon^{-\frac{\varphi_0 e}{kT}}.$$

The proper procedure in determining φ for temperature T is to determine φ_0 from the "T^2 equation" and then to add to this the quantity $(3/2)(k/e)T$. If instead, φ is evaluated from the "$T^{1/2}$ equation" what one obtains is an average value of $(\varphi_0 + (3/2)(k/e)T)$ for the range of the measurements. The difference between these quantities in the present measurements is comparable with the experimental error in determining the slopes of the straight lines. It seems, therefore, that the measurements have been made in accordance with the requirements of the classical theory, and that a better agreement was to have been expected than has been obtained.

It is generally recognized, however, that while the classical theory affords a satisfactory explanation of thermionic emission, and has one or two other notable achievements to its credit, it affords on the whole an unsatisfactory account of the electrical and thermal properties of metals. We should consider, therefore, whether a different theory may be expected to lead to a different set of thermionic relationships. This question has been considered by Richardson[1] who finds that differences are to be expected, and these, it appears, may very well be of a sort to account for the discrepancy we find between the differently determined values of φ. If we assume, for example, that the conduction electrons in a metal possess no thermal energy whatever, then the heat absorbed per electron leaving the surface of a filament is a measure of $\varphi e + 2kT$, the work done against electrical forces plus the thermal energy which the emitted electron is known from direct experiment to possess.

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[1] O. W. Richardson, "The Emission of Electricity from Hot Bodies," 1st ed., p. 169; 2d ed., p. 185.

Consistent with this we must suppose, in the derivation of Richardson's equation, that when a system consisting of an enclosure containing a body in equilibrium with its electron atmosphere at temperature T undergoes an isothermal expansion v, the heat absorbed is $nv(\varphi e + (3/2)kT) + pv$, instead of the same expression with the $(3/2)kT$ term omitted. This term does not appear on the classical theory because the average thermal energy of the electrons is supposed the same inside as outside the metal, ($(3/2)kT$ in each case). The difference that this makes in the interpretation of Richardson's "$T^{1/2}$ equation" is that the measured value of φ, which we will now refer to as φ_1, is no longer the equivalent of work done against electrical forces but that $\varphi_1 = \varphi + (3/2)(k/e)T$, where φ is this equivalent. This gives at once a reasonable explanation of the required variation of φ_1 with temperature, that is, of the relation

$$\varphi_1 = \varphi_0 + \frac{3}{2}\frac{k}{e}T.$$

On the present theory φ_0 is identified with φ, and this term alone represents work done against electrical forces. The second term is, in a sense, a proper part of the work function, but it does not represent a linear increase in the restraining voltage with temperature. Another alteration is that the approximation in the expression for φ_1 is no longer confined to the second term, so that, φ_0 (or φ) may vary somewhat with temperature.

What this means in connection with the present experimental results is that the equivalent voltage of work done against electrical forces alone is obtained by subtracting $2(k/e)T$ from the calorimetric value of φ, or $(3/2)(k/e)T$ from the value calculated from the temperature-emission relation. Making these subtractions for $T = 2270°$ K., we have

$$\varphi = 4.91 - 0.391 = 4.52 \text{ volts (calorimetric)}$$

$$\varphi = 4.778 - 0.293 = 4.48 \text{ volts (temperature-emission)}$$

i.e., values of φ are obtained differing by less than one per cent.

While it may be reading too much into the results to say that they differentiate between the two theories in favor of the view that the conduction electrons in metals possess little or no thermal energy, it may at least be said that they are more consistent with this view than with the classical theory.

It may be cited as further evidence in support of this view that our value of φ by the calorimetric method is in better agreement with that of H. H. Lester on the non-classical than on the classical theory. Lester's value, 4.478 volts, was obtained by subtracting $2k/e(T - T_0)$ from the total equivalent of the energy absorbed per electron. This should be the correct value on the classical theory. On the non-classical theory the quantity subtracted would have been $2k/eT$, giving $\varphi = 4.438$ volts. The agreement between our value of φ and Lester's is thus better on the latter theory. This will be clearer perhaps if all of the figures are set down together.

	Lester.	D. & G.	Diff.
Classical theory	$\varphi = 4.478$	4.91	9.6%
Non-classical theory	$\varphi = 4.438$	4.52	1.9%

There is some difficulty, of course, in understanding how it is that, if the conduction electrons in a metal do not possess normal thermal energy, they nevertheless escape from the surface with the average energy $2kT$. The way out of this difficulty may be contained in Borelius'[1] suggestion that while the conduction electrons in the body of a metal possess only a small fraction of normal thermal energy those near the surface possess the normal amount.

In connection with some more recent work we have been led to the consideration of quite a different possible explanation of the difference between the values of φ found by the two methods. As this cannot well be taken up here it will be presented in a later publication.

We take pleasure in expressing our thanks to Mr. R. E. A. Putnam of this laboratory who contributed much in preliminary experiments to the development of the present calorimetric method, and to Drs. H. D. Arnold and W. Wilson for the interest they have taken in this work, and for the encouragement they have given us.

Research Laboratories of the
American Telephone and Telegraph Company,
and the Western Electric Company, Incorporated.
Feb. 1, 1922.

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[1] Phil. Mag., 40, p. 746 (1920).

THE RELATIVE SENSITIVITY OF THE EAR AT DIFFERENT LEVELS OF LOUDNESS.

By Donald MacKenzie.

Synopsis.

Alternation Phonometer for Balancing the Loudness of Tones of Different Pitch.—It has been found that if two tones alternate in the ear at a suitable rate, for instance 25 times a second, the interruptions of the louder tone are the more conspicuous, and it is possible to adjust the relative intensities until the interruptions are equally conspicuous. Two tones when balanced in this way are said to be equally loud. This definition is justified by the fact that if two tones each balance a third tone they are found to balance each other and are also accepted by the ear as equally loud. The electrical circuit, commutating relays, and other apparatus used in making a loudness balance are described. To enable the mean pressure of the sound at the ear drum to be calculated from the electrical energy input, either a thermophone, whose theory is known, or an electromagnetic receiver which had been calibrated (rather imperfectly) by means of an artificial ear cavity and an electrostatic transmitter, was used next the ear. Successive readings usually agree within 5 per cent.

Relative Sensitivity and Sensibility of the Ear, at Various Loudness Levels, for Frequencies of from 100 to 4,000 per Second.—(1) Phonometric comparisons with a thermal receiver were made by ten men and ten women over a limited range of loudness. The results correspond to the equation $\log P_1 = A + B \log P_2$, where P_1 and P_2 are the acoustic pressures, computed from the thermophone theory, of the two balanced tones. This equation is in harmony with Fechner's law. The constant $-A$ is the sensitivity and depends only on the threshold pressures; $1/B$ is the relative sensibility at the two frequencies and is found to be constant, within 10 per cent., for the entire range of frequencies investigated. The curves for men and for women show no systematic differences except at the higher frequencies where resonance of the ear cavity begins to enter. (2) With an electromagnetic receiver a greater loudness range was possible, the pressure being varied up to 20,000 times the threshold values. Of 32 curves obtained with four observers making comparisons against 700 cycles, 25 were straight throughout, in agreement with the thermophone results, and only 7 were distinctly curved near the extremes. The slope at all frequencies is between 0.9 and 1.0; therefore the sensibility is practically uniform, at least to 2,000 cycles and at all loudness levels. No evidence of a phonometric Purkinje effect was observed, but it may be present for pressures near the threshold values. Since the pressures are all computed, the absolute values of A probably contain small systematic errors, but these would not affect the values of B.

INVESTIGATIONS of the sensitivity of the ear at the threshold of audition enjoy the advantage of dealing with one frequency at a time. If it is desired to study ear sensitivity at higher levels, means must be devised for the adjustment of different frequencies to equality of loudness. This done, data may be obtained showing physical intensities of sounds which to the ear are equally loud.

Methods of Sound Comparisons.

The customary method of making loudness balances is to listen to one frequency, then to the other, changing the intensities until the sounds are accepted as equally loud. This measurement can be made with some precision when the sound sources compared are emitting the same note, but is highly uncertain with two notes of different pitches. Aside from the flagging of the attention, there occurs a decay of the sensation,—the mechanism which appreciates loudness is fatigued as the sound continues. Presumably, a different mechanism responds to the second frequency, and the comparison made is between a decayed response to f_1 and a fresh response to f_2. This decay of sensation is readily observed by listening to a steady tone which suffers from time to time interruption for a perceptible interval,—after each interruption the sound seems louder, although the physical intensity has not altered.

It might be affirmed that such an error is offset by the opposite error when the order of the compared frequencies is reversed. In point of fact, however, each change leaves the ear in doubt, and the continuance of the work results in fatigue of all the auditory mechanisms involved. The net result is confusion and the impossibility of obtaining consistent observations.

In optical work, the flicker photometer has made it possible to compare the brightnesses of different colors. A flicker frequency is obtainable such that the colors fuse subjectively, and fluctuations in intensity, as well as the distinction of color, disappear at a definite brightness ratio of the colors compared.

A mechanically operated device, termed a flicker phonometer, has been patented by Heck.[1] The essential feature of this invention, as disclosed in the patent, is a sound-insulated valve automatically rotated at adjustable speed. Two tubes separately receive the sounds it is desired to compare, and each tube conveys an acoustic wave to the rotating valve, by which one tube is opened as the other is closed. Through the valve the tubes discharge sound to horns movable on a track, each facing the inlet to a tube leading to the ear. The claim is made that by proper disposition of the horns and regulation of the valve, pulsations in intensity of the sound reaching the ear can be caused to disappear. It is not apparent that the inventor contemplated the comparison of sounds of widely different pitches.

In this laboratory it has been found possible by electrical means to make use of the perception of flicker in an alternation phonometer. Let two frequencies alternate in the ear at a suitable rate, the intensity of one being maintained constant while the other is varied from faint to loud in comparison. The strong tone is heard plainly interrupted, accompanied by the weaker tone whose interruptions are not clearly distinguished. If now the weak tone is progressively strengthened, its interruptions begin to claim the observer's attention and with further increase in intensity come to overshadow the constant tone just as they were previously overshadowed when faint. A little practice enables the observer to determine a point at which the ear recognizes the two tones as equally interrupted: the attention is here impartially divided, whereas on either side of this point one or the other of the tones makes the stronger impression. Such a point may be identified with a loudness balance.

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[1] Method and Apparatus for Comparing Sounds, C. M. Heck: U. S. Pat. No. 1,356,359, October 19, 1920.

This statement is justified by the following considerations: (1) unpracticed observers can reproduce their balances within 4 per cent.; (2) on comparing in the usual manner the tones so equated, it is not possible to affirm which is the louder; (3) if in this way f_1 is compared with f_2, and the value of f_2 just found is balanced in turn against f_3, then f_1 and f_3 have values which on direct comparison are found to balance.

Comparisons of this kind avoid difficulties due to the shortness of the persistence of audition and to ear-fatigue. It is, moreover, plausible to urge that the level of any sensation is specified by the attention paid to the stimulus, and it is on this basis that the alternation phonometer is operated.

The Alternation Phonometer.

The currents furnished by two oscillators are alternately impressed on an electrical generator of sound by the armature of a polarized telegraph relay, driven from another such relay at a controllable speed. The relays and their operating circuit are shown in Fig. 1. The use of these relays and the circuit of Fig. 1 were suggested by Dr. W. S. Gorton of this laboratory.

Adjustment is carefully made to secure (within 1 per cent.) equality of duration of contacts on the two sides, and travel time between contacts not greater than 0.002 second. This travel time should not be exceeded, it being desirable to avoid intervals of silence. Within this limit, available sounding intervals range from 0.020 to 0.080 second. An interval of 0.040 second is suitable for frequencies 100 to 4000.

The currents commutated by the driven relay are amplified and supplied either to a gold-leaf thermophone or to an electromagnetic receiver. Fig. 2 is a diagram of the circuit between the relay commutator and the sound generators.

Specimen Results.

In preliminary experiments the procedure was to keep fixed the intensity of one of the tones and vary the other until a balance was reached. Comparisons with the thermophone were made by one observer of a large number of frequencies from 100 to 4,000 cycles. The r.m.s. alternating pressures in the cavity consisting of the thermophone case and the ear canal were computed from a theoretical formula developed by Dr. E. C. Wente.[1]

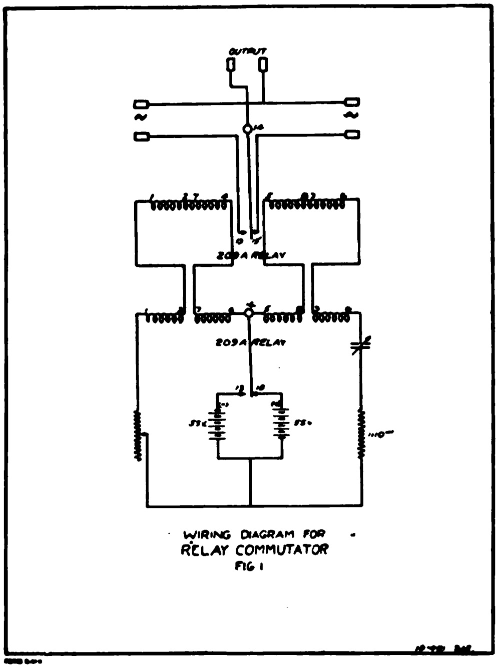

Fig. 1.

If we compare 400 vs. 500, 500 vs. 600, we can infer the result of a direct comparison of 400 vs. 600. Call p_1 the r.m.s. alternating pressure due to a frequency f_1 balanced by p_2 due to f_2, p_3 due to f_3. For the case where $f_1 = 400$, $f_2 = 500$, $f_3 = 600$, we find the following results:

TABLE I.

Observer: T. J. E.

Fixed in Volume.		Varied in Volume.	$\frac{\text{Varied}}{\text{Fixed}}$, Ratio of Pressures at Balance.
400 (f_1)	*vs.*	500	0.76
400	*vs.*	600	0.66
500 (f_2)	*vs.*	400	1.33
500	*vs.*	600	0.84
600 (f_3)	*vs.*	400	1.70
600	*vs.*	500	1.22

Here

$$\frac{p_1}{p_2} = 1.33; \qquad \frac{p_2}{p_3} = 1.22; \qquad \therefore \frac{p_1}{p_3} = 1.62.$$

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[1] "The Thermophone," PHYS. REV., 19, pp. 333–345, April, 1922.

By direct comparison,

$$\frac{p_1}{p_3} = 1.70.$$

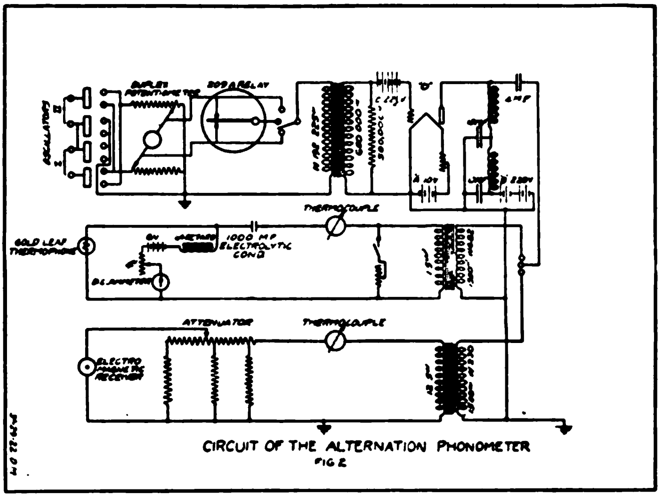

Fig. 2.

Again, when the frequencies exchange rôles, the one previously maintained at fixed volume becoming the variable, we find

$$\frac{p_2}{p_1} = 0.76; \qquad \frac{p_3}{p_2} = 0.84; \qquad \therefore \frac{p_3}{p_1} = 0.64.$$

By direct comparison,

$$\frac{p_3}{p_1} = 0.66.$$

The question arises, does the pressure-ratio at balance vary with the absolute sensation level? To answer this, comparisons of 100 vs. 300 were made at pressures ranging from 1 to 8 dynes/cm.^{2} for 300, 2 to 26 dynes/cm.^{2} for 100. Figs. 3 and 4 are curves representing these data, obtained by two observers.

The data of one observer are plotted in the upper curve of Fig. 3. The lower curve of this figure represents data taken by the same observer, comparing the same frequencies, on the following day. In the second case, a slower rate of commutation was used, the higher speed being judged too high for satisfactory perception of the 100-cycle tone.

The computed points are obtained from a law suggested by a logarithmic plot. It is seen that there is good agreement between the points so computed and those actually observed.

CONCORDANCE WITH FECHNER'S LAW.

Ab initio, we should feel no surprise at finding a logarithmic law. If we are working at a sensation level within the range of Fechner's law, the sensation should be connected with the stimulus (in this case loudness with pressure) by the relation

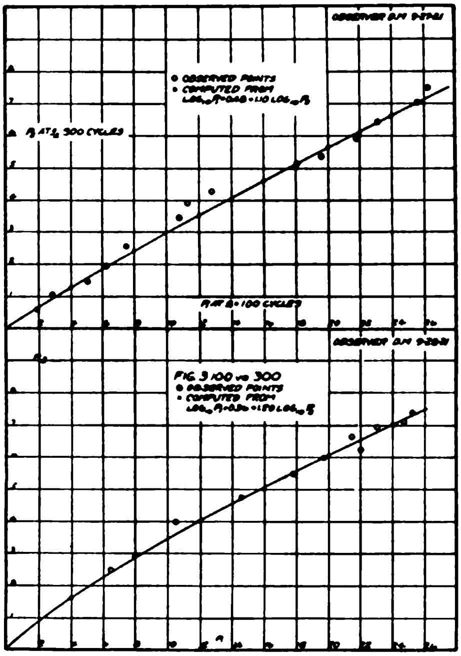

Fig. 3.

$$S = c \log P + a.$$

When two frequencies are at the same loudness,

$$S = c_1 \log P_1 + a_1 = c_2 \log P_2 + a_2$$

or

$$\log P_1 = \frac{a_2 - a_1}{c_1} + \frac{c_2}{c_1} \log P_2.$$

Within the range of validity of such a law, then, we should expect the balances to obey a law of the form

$$\log P_1 = A + B \log P_2.$$

Further evidence confirmed this expectation. Fig. 4 shows logarithmic plots of the data of another observer (T.J.E.) comparing 100 *vs.* 200, 200 *vs.* 300, 100 *vs.* 300. The logarithmic law satisfies observations on frequencies from 100 to 4,000.

At the higher frequencies (2,000 to 4,000) difficulties were found in checking indirect with direct comparisons. If the thermophone case is not held tightly against the ear, a small opening converts the cavity into a Helmholtz resonator and so enhances the effect of the tone whose frequency is the nearer to the natural frequency of the resonating cavity. This source of error may be precluded by care in manipulation. An additional uncertainty is introduced by harmonics contaminating the tones,—this difficulty is remedied by the introduction of filters. Failure to check direct against indirect comparisons may also be due to omitting the precaution to make comparisons at a fixed sensation level.

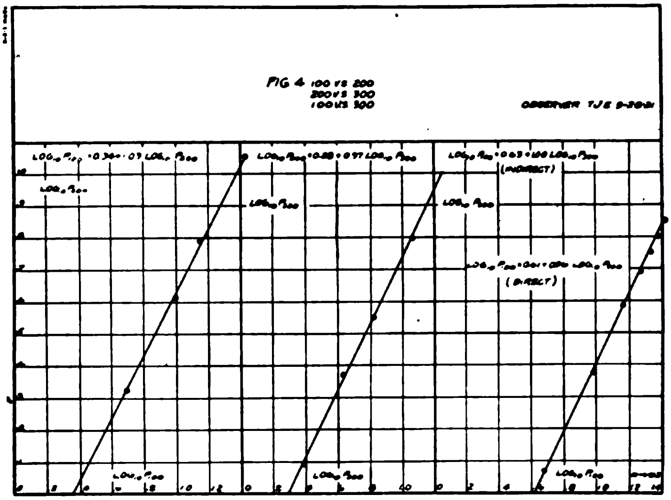

Fig. 4.

When care is taken to conform to these three specifications (tight fit of thermophone against ear, purity of tones compared, fixed level of sensation), the discordance between direct and indirect comparisons is small.

The introduction of a duplex potentiometer, reducing one tone as the other is increased, enables the observations to be made more rapidly and with greater confidence. After each balance, the relays are stopped and the necessary current readings taken. In addition, the observer is given an opportunity to compare the loudnesses of the tones he has adjusted and is asked if his ear accepts them as equal. In nearly every case he finds no fault with the balance. The oscillators are then interchanged on the potentiometer and the observation repeated; the average of the two settings is plotted. A discordance as great as 5 per cent. is uncommon, and does not occur in the absence of distracting room noises.

Suitable changes in currents enable four pairs of balances to be made at levels such that the corresponding points are uniformly spaced on a logarithmic plot.

EAR SURVEYS WITH THERMOPHONE.

A survey of 20 ears (of 10 men and 10 women) was carried out with the thermophone. Comparisons were made at four levels involving the frequencies 100 (or 120), 200, 300, 500, 700, 1,000, 1,500, 2,000, 3,000 and 4,000 cycles. Time did not permit all possible combinations, hence in several cases comparisons were made of widely separated frequencies in order to test the claim that direct comparisons may be inferred from indirect.

Of 180 comparisons made by the 20 observers, the results in 93 cases fitted logarithmic straight lines to within the error of the current measurements. No systematic deviations, either for men or women, were found in the other cases. Accordingly, the occasional wide deviations were attributed to experimental blunders. In view of the general confidence in Fechner's law and the concordance with it of most of the results of this survey, the logarithmic equation seems satisfactory.

As an illustration, the results obtained by one observer are given in the table below:

TABLE II.

Observer: F. H. G.

$\log_{10} P_1 = A + B \log_{10} P_2$.

	f_1.	f_2.	A.	B.
(1).........	100	300	0.63	.92
(2).........	200	300	.19	1.00
(3).........	300	500	.30	1.04
(4).........	500	700	.21	.97
(5).........	700	1000	.14	.97
(6).........	1000	1500	.30	1.02
(7).........	1500	2000	.08	.96
(8).........	2000	3000	.13	.93
(9).........	3000	4000	.28	.90
	200	3000	1.41	.91 direct
	200	3000	1.34	.91 indirect combining (2)-(3)-(4)-(5)-(6)-(7)-(8)

Weighting the observations equally, we plot in Fig. 5 the averages of all. For each comparison four circles, each the average of 20 settings, represent the observations by the men; four crosses, those by the women.

It is apparent that the averages fit logarithmic straight lines closely and that there is no certain difference between circles and crosses, except in the comparisons of 2,000 and 4,000 against 3,000. It is near these frequencies that resonance is to be expected. The canal and the ear cavity have been taken in the pressure computations as of the *average* length and volume; for this reason the circles and the crosses would fail to coincide at frequencies near resonance should there be between men and women a systematic difference in shape of ear cavity.

Table III. is a condensed tabulation of the results obtained. The separate comparisons have been reduced to 700 cycles as reference frequency.

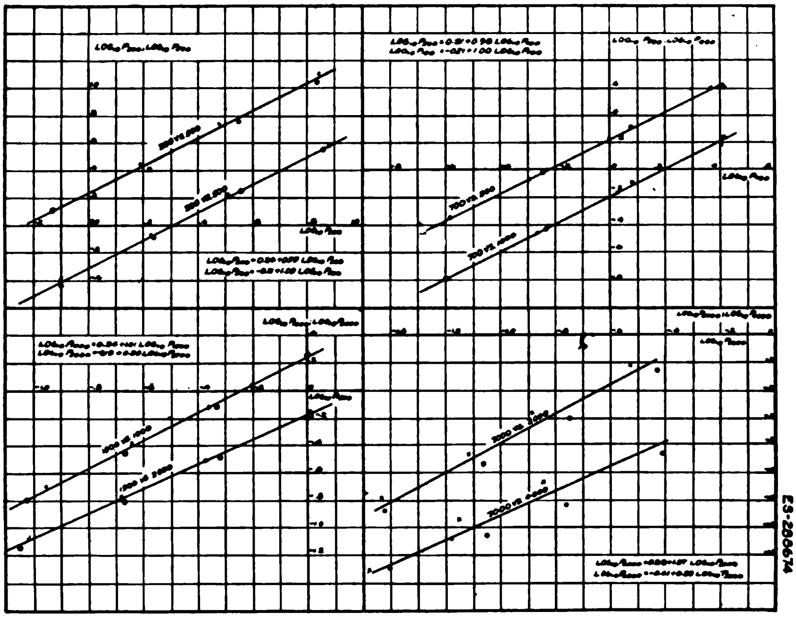

FIG.5 RESULTS OF THERMOPHONE COMPARISONS

Fig. 5.

TABLE III.

$\log_{10} P_f = A + B \log_{10} P_{700}$.

f.	*A.*	*B.*	Individual Extremes.	
			A.	*B.*
200.......	0.76	0.97	0.57, .96	0.62, 1.42
300.......	0.52	.98	.41, .65	.59, 1.18
500.......	0.21	.98	.14, .33	.77, 1.10
700.......	0.00	1.00	— —	— —
1,000.......	−0.21	1.00	− .29, −.09	.83, 1.29
1,500.......	−0.45	.99	− .66, −.33	.80, 1.22
2,000.......	−0.60	.89	− .81, −.38	.62, 1.09
3,000.......	−0.82	.84	−1.40, −.50	.63, 1.14
4,000.......	−1.14	.74	−1.67, −.79	.39, 1.37

RELATIVE SENSITIVITY OF THE EAR.

It is convenient to regard the data, taken all together, as yielding a determination of the acoustic pressures which phonometrically balance the pressure of 1 dyne per sq. cm. at 700 cycles. The reciprocals of these pressures express the relative ear sensitivity. The frequency of 700 cycles is chosen as standard because it is the last audible frequency in the average voice progressively attenuated, and the reference value of pressure roughly corresponds to the band of average speech between 600 and 800 cycles.

In Fig. 6, curve A is the ear *sensitivity* referred to the standard just described. The ordinates of this curve are the negatives of the values of A in Table III.; frequencies on the musical scale are plotted as abscissæ.

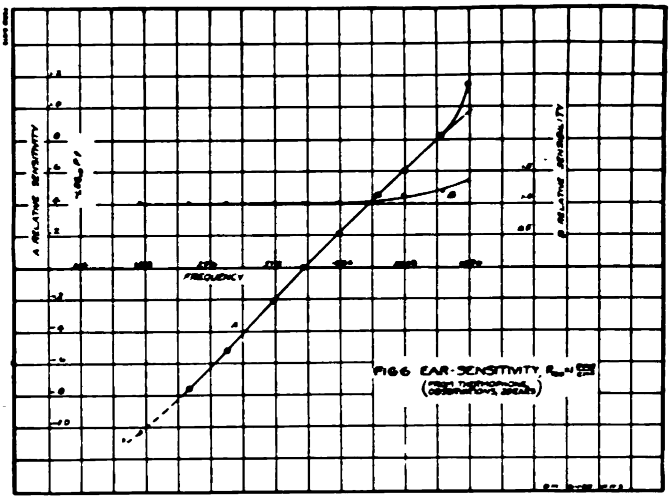

Fig. 6.

Values of B in Table III. show the change in log P_f required to maintain the phonometric balance when log P_{700} changes by unity. Reciprocals of the B's therefore exhibit the ear *sensibility* referred to 700 cycles: curve B, Fig. 6.

It is to be emphasized that the alternating pressures generated by the thermophone are obtained from computation. As yet no method has been devised for the immediate measurement of pressures on the ear drum, or for studying the reaction of the air chamber and walls of the ear on the thermophone. Until such ideal measurement is possible, the values of A cannot be guaranteed free from systematic errors. Probably these errors are small, and below 2,000 cycles do not greatly vary with frequency. The abrupt turn in curve A, Fig. 6, may be due either to resonance of the air cavity or to resonance of the drum.

The value of B, on the other hand, should be unaffected by an uncertainty in that of A, provided only the acoustic output of the sound generator be proportional to the electrical input. It will be noted that up to 1,500 cycles, the relative *sensibility* is unity, but increases appreciably to 1.35 at 4,000 cycles. Reëxamination of the data discloses the fact that if we exclude those observers whose comparisons above 1,000 cycles were in any case erratic, we have left eight ears out of twenty for which the values of B lie between 0.9 and 1.1. The indirect comparison of 4,000 and 700 involves five steps: blunders or errors in any one of these distort the series of B's for the ear concerned. It appears reasonable, therefore, to take the sensibility as uniform over the frequency range covered.[1]

In Fig. 6 observations at 100 cycles by 8 men and at 120 cycles by the 10 women are represented by crosses, to which the curve A is tentatively extended.

The advantages of the thermophone as a sound generator are convenience of computation and practical absence of transients. A serious disadvantage is the narrowness of the available range of loudness. The extremes of pressure within which the ear can accommodate are in the ratio 10^6 to 1; the thermophone surveys cover only one-sixth of this range, the pressure limits being 10 to 1. Conceivably, the simple law valid within these limits may fail outside them.

Extension of Loudness Range.

Wider limits were reached by the use of an air-damped electromagnetic receiver in place of the thermophone. The supply circuit of the receiver includes an attenuator, as shown in Fig. 2. The dial of the attenuator is marked in "napiers": the introduction of N napiers reduces the voltage at the receiver terminals to e^{-N} times its former value. On this account it is convenient to express the sound output of the receiver in napiers (natural logarithms of the pressures).

The unattenuated sound emitted by the receiver is as loud as the ear can tolerate without discomfort. With the attenuator the tone can be reduced to inaudibility.

The electromagnetic receiver is calibrated in terms of acoustic pressure per volt input at the frequencies selected for the phonometer comparisons.

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[1] This conclusion is confirmed by V. O. Knudsen, who finds the sensibility nearly independent of the frequency between 100 and 4,000 cycles: "Sensibility of the Ear to Small Differences in Intensity and Frequency" (abstract), Phys. Rev., 19, p. 261, Mar., 1922.

An "artificial ear," coupling the receiver and an electrostatic transmitter-amplifier system, enables the calibration to be made as follows:

An alternating voltage of a given frequency and appropriate magnitude is impressed on the receiver terminals and the corresponding amplifier output noted. The receiver is then silenced and a known voltage of the same frequency introduced into the amplifier input in series with the electrostatic transmitter. Comparison of the amplifier output in this case with that due to sound pressure on the transmitter diaphragm, together with the dynamical characteristic of the transmitter, permits computation of the sound pressure corresponding to the alternating voltage on the receiver. The artificial ear is intended to simulate the real ear in respect to volume and mechanical reaction on the receiver diaphragm. Were this simulation perfect, the observations just described would enable us to compute the pressures on the ear-drum when the receiver is held against the ear.

However, the simulation is far from perfect. The real ear affects the motion of the receiver in a way which the artificial ear imitates fairly well over the central region of the frequency range. But the cylindrical cavity and the rigid walls of the artificial ear differ greatly from the comparatively soft walls of the curved auditory canal and external ear, and the artificial ear fails at high and at low frequencies.

We have, then, a calibration of the electromagnetic receiver under conditions which differ from those of use, and the results of work with such a sound generator can not be stated in ideally accurate numerical values.

It is, however, permissible to use the receiver without the perfect calibration. Provided the pressure output of the receiver is proportional to the voltage at its terminals, and provided further that this voltage is known, it is possible to study variations in relative sensitivity as the loudness varies between wide limits.

Both requirements mentioned above may be incompletely satisfied. At high levels the receiver may be overloaded and the sound output cease to be proportional to the voltage. At low levels, where great attenuation is introduced, the impedance of parasite current paths may no longer be large in comparison with that of the network in the attenuator and the voltage at the receiver terminals may be incorrectly deduced from the dial setting. Such parasite paths are offered by capacity between input and output, due to conductors in the vicinity of the attenuator, and by induction owing to inadequate shielding of input and output leads. Care was taken to place and shield the leads safely, but it was desirable to determine how successfully this was done.

The proportionality of sound output to impressed voltage is tested by bringing the receiver up to the transmitter-amplifier and reading amplifier output currents for alternating voltages corresponding to attenuator settings from 0 to 4 napiers. As in the calibration of the receiver, voltages in the transmitter are determined. By reason of the great stiffness and small motion of the transmitter diaphragm, it is proper to assume proportionality of acoustic pressure and voltage generated in the transmitter. It is clear that the load characteristic of the receiver can be derived.

It was found that a correction on this account was not required above 200 cycles. The amplitude of the receiver diaphragm is greatest, and so overloading most easy, at the low frequencies. In the curves later shown the correction at 200 has been applied.

Parasite current paths, the existence of which leads to incorrect estimates of receiver voltage, are important only at low levels. Let the current input to the attenuator be the maximum permissible, and let N_1 be the dial setting necessary to reduce the sound output to the threshold. Now let the input current be reduced in the ratio $1 : e$; N_2 is the new threshold setting. When the parasite paths are negligible, $N_1 - N_2 = 1.0$. The threshold for any individual ear varies from day to day, but is sensibly constant over the few minutes required for this test.

Such an examination failed (for any of the frequencies here considered) to indicate errors exceeding a tenth of a napier,—an admissible experimental error.

PHONOMETRIC COMPARISONS WITH ELECTROMAGNETIC RECEIVER.

Following these studies of the receiver, phonometric comparisons were undertaken by four observers. These comparisons with the electromagnetic receiver extended from 1 or 2 to 10 napiers above the threshold, taking 700 cycles as the reference tone. Each of the other tones was compared directly with 700, avoiding the objectionable features of indirect comparisons.

Before presenting the results obtained, it is profitable to consider what types of curves are to be expected in ideal phonometric comparisons covering a wide range of loudness.

Fig. 7, *I*, shows hypothetical Fechner curves, relating stimulus and "sensation," for the frequencies f_1 and f_2. Such curves for the ear have not yet been determined by experiment, but in drawing the hypothetical figures analogy between eye and ear has been presupposed.

Fechner curves for vision are constructed by integrating curves of sensibility (reciprocal of least perceptible stimulus increment) *vs.* logarithm of stimulus. Each curve contains (1) a curved portion at low intensities, concave toward the axis of sensation; (2) a straight portion, throughout which the least perceptible stimulus increment is constant; (3) another curved portion at high levels, concave toward the axis of log stimulus. At each end of the straight portion the curve bends because the least perceptible stimulus increment is no longer constant. Implicit in the construction of these curves is the assumption that whatever be the least perceptible change in the stimulus the accompanying change in the sensation is of invariable amount.

The sensation scale is undetermined, but we can imagine that by an ideal loudness balance, say at the level "*a*," coincidence of the scales for f_1 and f_2 has been established.

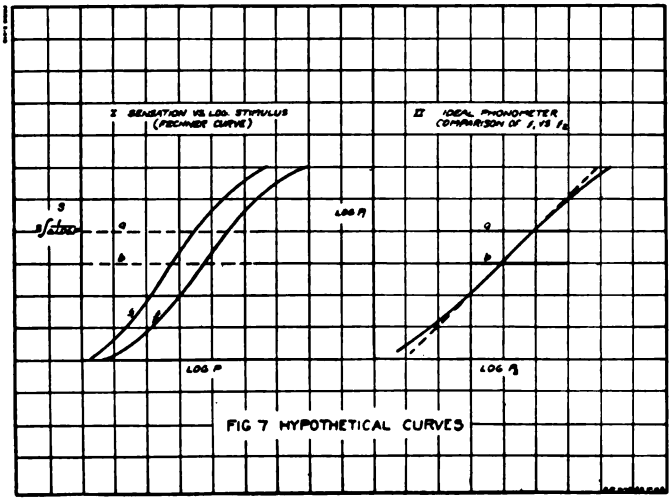

Fig. 7.

If phonometric comparisons are made of the tones represented by these curves, we shall obtain pairs of values of log P_1 and log P_2,—each pair will correspond to a definite sensation level, say "*a*" or "*b*." Fig. 7, *II*, shows, in the full line, the ideal phonometer results. In the figure to the left, the curves for f_1 and f_2 start from different thresholds and have different curvatures in the upper and lower portions. Centrally, where each curve is straight, phonometric comparisons will give a straight line for log P_1 *vs.* log P_2. If the slopes of the straight-line portions are the same, the slope of the phonometric line will be unity within these limits. At levels of loudness above "*a*" or below "*b*" however, the phonometric line will be curved as drawn. Were the sensation-stimulus curves at all ordinates uniformly spaced in abscissae, the phonometer would give the dotted line at 45°, coincident in the middle of the range with the full line.

Individual ears may be expected to vary in several respects. The threshold values of stimulus intensity vary with frequency for a given observer, and at each frequency differ with different ears. The values of stimulus intensity at which the Fechner curves become straight lines, and the stimulus intervals within which the lines remain straight, vary among frequencies for each observer and among observers for each frequency. Moreover, the characteristics of the ear change from day to day.

From the foregoing discussion, it is clear that we may expect two types of phonometric curves, provided the analogy holds between the eye and the ear. The types are (1) straight lines over a considerable range; (2) sharply curved lines of which the upper and lower halves are of opposite curvature. Lines of intermediate shapes will of course occur.

The observers who took part in the studies with the electromagnetic receiver are too few in number to make us sure that individual pecularities will be masked in the final average. Besides, the observing program covered six or eight hours for each ear (as against two or three hours in the thermophone surveys) and in three cases the observer was prevented from completing the program the same day he began it. It is therefore desirable to discuss the comparisons separately.

On examination, it was found that the observer who concluded the program in a single day obtained, for all comparisons, sensibly straight lines over the entire range. The three other observers obtained straight lines in most comparisons, but also a number of sharply curved lines of the second type anticipated above.

The distribution of these types and the general aspect of the data may be seen from Table IV. in which are tabulated the frequencies (each compared directly with 700 cycles) and the corresponding numbers of lines of each type.

Table IV.

f.	Sensibly Straight.	Sharply Curved.
200	4	0
300	3	1
500	4	0
1,000	2	2
1,500	2	2
2,000	4	0
3,000	3	1
4,000	3	1
	25	7

The preponderance of straight lines is unmistakable. In Fig. 8, at the left, the sensibly straight lines for each frequency are consolidated into an average line; at the right are drawn the individual curves which conspicuously depart from straightness.

Threshold settings were made for each frequency. These are plotted in Fig. 8 and the phonometer curves extended to them. The curves suggest that the auditory accommodation taking place in the comparisons is the same as at the threshold.[1]

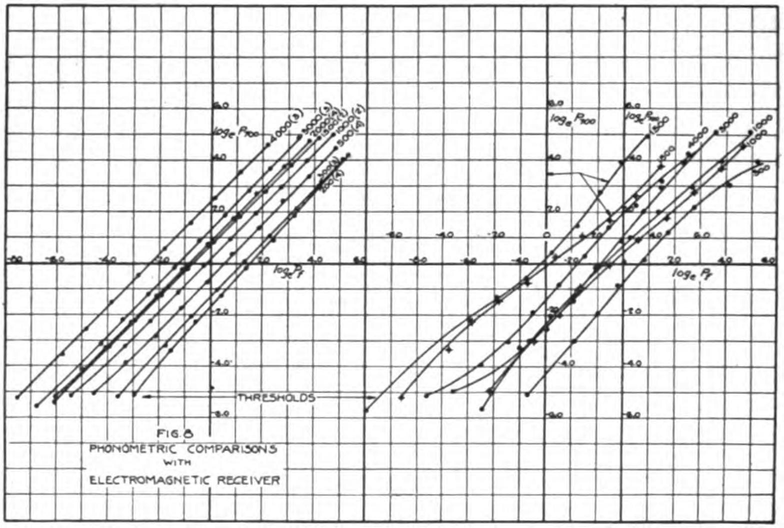

Fig. 8.

A short study was made by one observer, making on different days repeated comparisons of the same two tones. As might be expected, it was found that the curve obtained varied from straight on one day to curved on the next.

Care was taken by two observers to make a partial check of the validity of the phonometric technique by comparing two sounds of the same frequency (700 cycles). Whatever the calibration of the apparatus, equality of loudness in this case should mean equality of currents through the two contacts of the commutating relay. The greatest deviation from equality was 10 per cent. This occurred at the highest level; at intermediate and low levels the deviations were too small to be detected.

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[1] The threshold sensitivity derived from these settings differs only at 3,000 and 4,000 cycles from that given by Fletcher and Wegel ("The Frequency-Sensitivity of Normal Ears," Proc. Nat. Acad. Sci., 8, 1, pp. 5–6, January, 1922). The discrepancy is no greater than the uncertainty of the receiver calibration, ascribed to resonance in the ear near these frequencies.

Relative Ear Sensitivity at Different Levels of Loudness.

Without regard to shapes of individual curves, we plot the average curve of each comparison and scale off at various levels of the 700-cycle tone the values of log P for the other frequencies. Doing this at three levels ($\log_e P_{700} = -4.0, 0.0$, and $+4.0$) we plot the values of $\log_e P_f$ with reversed signs and so draw at each level a curve of relative sensitivity of the ear. These are exhibited in Fig. 9, where, as in Fig. 6, the abscissae are frequencies on the musical scale; the ordinates, $-\log_e P$, are indicative of the relative sensitivity.

Obviously, the defects of the receiver calibration affect all these curves in the same way. The straightness of most of the curves shown in Fig. 8, and the closeness of their slopes to unity, insure the parallelism of the curves of Fig. 9.

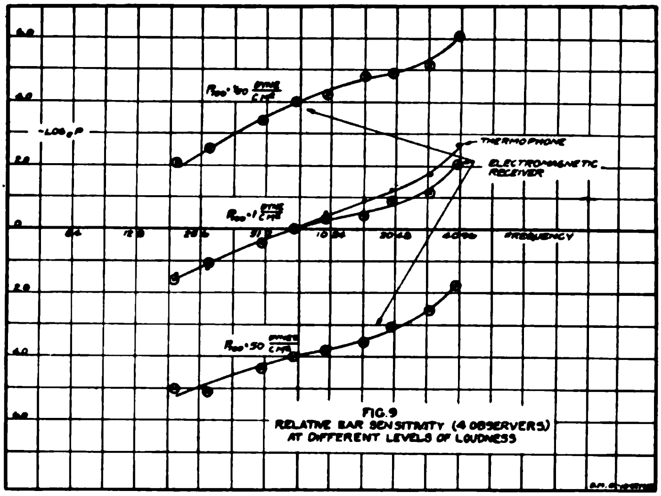

Fig. 9.

The calibration of the receiver and the computation of the thermophone output are both affected by unknown systematic errors. Numerous attempts were made to devise a method of comparing on the ear the sound output of the thermophone with that of the electromagnetic receiver. None of these attempts succeeded. Either the two sound generators must be interchanged on the ear or another receiver must be actuated by them alternately through the transmitter-amplifier system. In the first case it is impossible to make satisfactory comparisons, while in the second case the coupling to the transmitter sustains the uncertainty which the comparison is intended to remove.

As previously explained, the slopes of the lines should be unaffected by errors in the adopted sound pressure-frequency characteristic of either the thermophone or the electromagnetic receiver. From this point of view the two instruments agree: for the four observers using both, slopes by the thermophone over the central portion of the loudness range are 0.9 to 1.0; by the electromagnetic receiver, 0.9 at 200 *vs.* 700, 1.0 elsewhere.

SUMMARY.

1. At an intermediate level of loudness determinations with the thermophone have been made, by 20 observers, of the pressures of certain selected frequencies when these seem to the ear equally loud. The agreement among different ears is so close that improvement in the curve of relative sensitivity shown in Fig. 6 is to be looked for rather from verification of the pressure computations than from extending the survey to include a larger number of observers.

2. A limited number of observers have made observations over a range of loudness from 1 to 10 napiers above the threshold, using an electromagnetic receiver in place of the thermophone as source of sound. Their results are in general agreement with those obtained in the thermophone work, and strongly suggest that the relative ear sensitivity is invariable over this range.

3. The phonometric comparisons have been shown to be in harmony with Fechner's law, the application of this law to the ear being presumed valid.

4. The optical phenomenon known as the Purkinje effect has no analogue within the range of the phonometric comparisons. It is of great interest to continue this work at low intensities. In the present study, room noises made it impossible to work at levels near the threshold, where the Purkinje effect is perhaps to be found.

In conclusion, the results believed to have been accomplished may be thus stated:

I. A phonometer has been devised which permits accurate comparisons of the loudness of pure tones of different pitch.

II. With this instrument, evidence has been found that the relative sensitivity of the ear is independent of the loudness level over a wide range.

RESEARCH LABORATORIES OF THE AMERICAN TELEPHONE AND TELEGRAPH COMPANY,
AND THE WESTERN ELECTRIC COMPANY, INCORPORATED,
April 8, 1922.

THE OPTICAL PROPERTIES OF MOLTEN METALS.

By A. K. Aster.

Synopsis.

Optical Properties of Molten Bi, Pb, Sn, and Wood's Alloy to 500° and of Hg to 345° C.—While there is considerable evidence that the optical properties of metals in the solid state do not vary with temperature, the question has not yet been investigated for molten metals. A vacuum tight furnace enabled a nitrogen atmosphere to be used so that surfaces free from oxidation could be studied. The optical properties were determined by letting plane polarized light of wave-length about 6020 Å.U. fall at an angle of 45° upon the metal surface, and analyzing the reflected light with the help of a Jellet split nichol having a Brace elliptic half-shade mounted just before it. The method of calibration and use of the apparatus is described. The optical properties were found to be independent of the temperature for all the metals tried. The mean values, correct to better than one per cent., are as follows: for Bi, $\nu = 0.493$, $k = 1.32$; for Hg, $\nu = 0.442$, $k = 1.43$; for Pb, $\nu = 0.415$, $k = 1.76$; for Sn, $\nu = 0.398$, $k = 1.46$; for Wood's alloy, $\nu = 0.397$, $k = 1.78$. From a discussion it appears that the constancy of the optical properties is not consistent with Drude's equations.

Introduction and Previous Work.

THE optical properties of metals as a function of the temperature have been investigated to a certain extent for metals in the solid state. Kundt[1] investigated silver, antimony, copper, platinum, iron and nickel between 20 and 100 degrees C., using a direct method, employing thin metallic prisms. He found a slight variation of the index of refraction with the temperature. Drude[2] investigated gold and platinum up to 200 degrees C., and found only a very slight change in the index of refraction, but did not consider the work conclusive. Sissingh[3] investigated iron but did not find any change with the temperature. Zeeman[4] investigated platinum up to 800 degrees C., but did not find any change in the coefficient of reflection. Pfleuger[5] investigated nickel, gold and iron between 20 and 100 degrees C., by the same method as Kundt, direct observations on thin metallic prisms, and did not find any change with the temperature. Very little work has been done on metals in the molten state. C. V. Kent[6] investigated bismuth, cadmium, tin, and lead and their binary alloys. He did not definitely determine whether the optical properties were constant with the temperature or not and states in his paper that some work should be done to determine this point. His calculations are on the basis that the optical properties are constant.

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[1] Kundt, Wied. Ann., 36, 834, 1889.

[2] Drude, Wied. Ann., 39, 538, 1890.

[3] Sissingh, Arch. Nierlandaisses, tome XX.

[4] Zeeman, Comm. of the Phys. Lab. Leyden, 20, 1895.

[5] Pfleuger, Wied. Ann., 58, 493, 1896.

[6] Kent, Phys. Rev., XIV., 6, 495.

It was the object of this investigation to determine whether or not the optical properties of molten metals are functions of the temperature.

DESCRIPTION AND USE OF APPARATUS.

Various methods have been used for determining the constants of elliptically polarized light. The Babinet-compensator and the Babinet-Soleil modification of it have been used for large ellipticities while a more recent development, the Brace elliptic half-shade, has been used for small ellipticities. The apparatus used in this work is of the latter type. The arrangement used was similar to that used by A. Q. Tool[1] in his work on the optical properties of metals. The entire polarizing and analyzing systems were mounted in the arms of a vertical spectrometer especially constructed for the purpose. The polarizing system consisted of the usual collimator with a nicol prism mounted directly after the collimator lens. The analyzing system consisted of a compensator (mica between optical flats) mounted on a circle movable with respect to a fixed vernier and the analyzing nicol, a Jellet split nicol with an elliptic half-shade mounted just before it, was mounted on a second circle movable with respect to a vernier which was fixed with respect to the first circle. The half-shade was set with its dividing line at right angles to that of the split nicol. The entire analyzing system was mounted in the telescope arm of the spectrometer which was fitted with a short focus ocular. The spectrometer was fitted with a special device connecting the telescope and collimator arms so that when the collimator was set for a given angle of incidence the telescope was automatically set in the proper position for the reflected beam.

The source of light was a spectroscope fitted with a constant deviation prism and illuminated with an arc lamp using specially treated commercial carbons giving a strong band at approximately 6020 Å.U.

The theory of this analyzing system has been given by Tuckerman[2] in an article on elliptic analyzing systems. The procedure is to obtain a match of all four parts of the field and then make the complementary setting. Let R and r be the positions of the compensator and the nicol respectively for a match, and R' and r' for the complementary match and

$$R' - R = c,$$
$$r' - r = n;$$

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[1] Tool, PHYS. REV., XXXI., 1, 1.

[2] Tuckerman, Univ. of Neb. Studies, IX., 2, 157.

then if plane polarized light is let fall on the analyzing system, Tuckerman finds that

$$\cos 2\Pi N_1 = \frac{\tan c}{\tan n}, \tag{1}$$

$$\tan 2\eta = \sqrt{\frac{\sin (n - c) \sin (n + c)}{\sin c}}, \tag{2}$$

where 2η is the effective order of the half-shade and $2\Pi N_1$ is the order of the compensator. If the initial light is not plane polarized, he finds that

$$\tan 2\Pi N_1 = \sqrt{\frac{\sin (c - n)}{\sin (c + n)}} (1 - \alpha \tan 2\eta + 1/2\alpha^2 \tan^2 2\eta - \cdots), \tag{3}$$

$$\tan 2\psi = \sqrt{\frac{\sin (c - n) \sin (c + n)}{\sin n}} (1 - 1/2\alpha^2 \tan^2 2\eta - \cdots) \tag{4}$$

where

$$\alpha = \frac{\sin c}{\sqrt{\sin (c - n) \sin (c + n)}} \tag{5}$$

and if $2\gamma = (R' - R) - (R_0' - R_0) - 2\Phi$ and Φ is 45° as is customarily used, then

$$v_\theta = - \frac{\sin \Phi \tan \Phi \cos 2\psi \cos 2\psi}{1 - \cos 2\psi \sin 2\gamma}, \tag{6}$$

$$K_\theta = - \frac{\tan 2\psi}{\cos^2 \gamma}, \tag{7}$$

where R_0' and R_0 are the settings on plane polarized light,

v_θ = index of refraction,
K_θ = coefficient of absorption,
θ = angle of incidence.

By letting plane polarized light fall on the analyzing system, taking the necessary readings and applying equations 1 and 2, it is possible simultaneously to calibrate the compensator and the half-shade. By analyzing plane polarized light (for $\Phi = 45°$) when it is reflected from the metal surface and applying equations 4, 5, 6 and 7 the optical properties for that angle of incidence and wave length of light used, can be obtained.

Experimental Work.

The nicol prism of the polarizer was first adjusted for an azimuth of 45° by means of an auxiliary nicol. The compensator and elliptic half-shade were next simultaneously calibrated. This was done by setting the analyzer in direct line with the polarizer and making the two settings for a match. Substitution of the data thus obtained in equations 1 and 2 gives the following results:

$$\cos 2\Pi N_1 = 0, \qquad 2\Pi N_1 = 90^\circ,$$
$$\tan 2\eta = 0.366, \qquad 2\eta = 20.1^\circ.$$

A special vacuum-tight furnace was designed because in order to prevent oxides from forming on the surface of the molten metal it was necessary to have the furnace filled with nitrogen. A reducing atmosphere would probably have been better, but the risk of an explosion with the use of hydrogen was considered too great to warrant using it, so an inert gas was resorted to. Ordinary commercial nitrogen was found satisfactory. The commercial product contains about 5 per cent. of oxygen according to the manufacturer. In order to keep the amount of oxygen a minimum, the nitrogen was kept in the furnace at a pressure just high enough to prevent boiling of the metal. This pressure was from 20 to 30 cms. of mercury. The remaining oxygen was easily removed by skimming the metal a few times after it was molten, thus converting the oxygen to metallic oxide. After a few skimmings, it was possible to keep the surface clean for a considerable time. It should be stated at this point that the furnace was first exhausted before filling with nitrogen. It was also washed several times before the final filling with nitrogen, this being done to reduce the amount of oxygen to a minimum. This entire operation was completed before the furnace was heated to a point where the metal melted. It was necessary to have the furnace at least 25 degrees above the room temperature while exhausting it, in order to drive out most of the residual gas in the magnesia packing, etc.

The windows of the furnace were constructed of optical glass which was tested so as to be sure that it was free from optical strain. It was necessary to limit the observations to one angle of incidence (45°) in order that the entering and emerging light should always be normal to the plane of the windows to prevent introduction of errors. To be able to vary the angle of incidence it would have been necessary to reconstruct the major portion of the furnace housing for each angle. The furnace was mounted on a special anti-vibration mounting in order to prevent the vibration of the building from disturbing the surface of the molten metal while observations were being taken. This special mounting consisted of a box containing sand, on top of which were placed several marble plates separated by rubber stoppers. The furnace was set on top of the marble plates. The temperature of the metal was measured by means of a chromel-alumel thermocouple. The cold juncture was kept in a Dewar flask filled with distilled water, the temperature of which was measured with a good mercurial thermometer. A Leeds-Northup potentiometer type pyrometer indicator reading directly in millivolts was used as the indicator. The calibration of the couple was taken from data available in the laboratory. See Fig. 1 for a cross-section of the furnace.

A number of metals were investigated, the results of which are listed below. It was found impossible to continue the investigation above about 500 degrees C., as at this point the metal begins to glow a dull cherry red and this light masks the light from the collimator so that on further settings could be made. It was impossible to use filters as the two colors were nearly alike and any filter which would exclude the one beam would so reduce the other that it would be impossible to make accurate settings and in this sort of work it is necessary to have the maximum possible intensity so as to insure sufficient sensitivity of the apparatus. The sensitivity of the system drops off very rapidly with diminishing intensity. It was found impossible to make any determinations just at the melting point because at this point the metal surface is still rough. It was found necessary to raise the temperature at least about ten degrees above the melting point of the metal to get the metal liquid so as to get a smooth surface. How far one has to go above the melting point depends on the metal. It was found impossible to take any data above 345 degrees C. for mercury, because above this point the mercury vapor condensed on the windows of the furnace making it impossible to see through them. Two attempts were made to get data for cadmium but both were failures. In the first attempt, the cadmium combined with the graphite crucible, and it was impossible to get a clean surface. In the second trial an alundum crucible was substituted for the graphite one, but it was still found impossible to get a clean surface. (Ordinary chemically pure metals were used for all tests.)

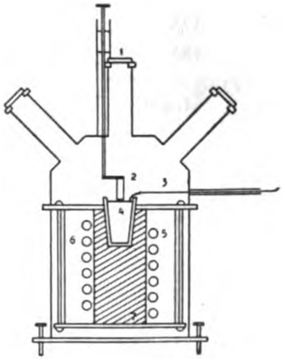

Fig. 1.

1, Glass window. 2, Stirrer. 3, Thermocouple. 4, Crucible and metal. 5, Heater conductor. 6, Magnesia packing. 7, Iron heater core.

RESULTS.

Lead.

Temp.	ν_θ.	K_θ.
335° C.	0.414	1.76
345	0.413	1.74
365	0.415	1.75
385	0.417	1.78
405	0.414	1.77
427	0.416	1.74
440	0.414	1.78
475	0.415	1.77
485	0.416	1.76
Mean	0.415±0.0006	1.76±0.005

Tin.

Temp.	ν_θ	K_θ.
250° C.	0.396	1.46
315	0.398	1.44
335	0.397	1.48
345	0.399	1.45
357	0.400	1.46
375	0.397	1.47
395	0.398	1.44
425	0.396	1.46
450	0.400	1.48
480	0.398	1.44
Mean	0.398±0.0005	1.46±0.0045

Bismuth.

Temp.	ν_θ.	K_θ.
275° C.	0.493	1.31
285	0.492	1.32
295	0.494	1.31
317	0.491	1.30
345	0.495	1.34
375	0.491	1.33
395	0.493	1.32
405	0.492	1.34
425	0.494	1.31
450	0.491	1.33
465	0.493	1.32
485	0.495	1.32
Mean	0.493±0.0005	1.32±0.006

Mercury.

Temp.	ν_θ.	κ_θ.
22° C.	0.441	1.42
65	0.442	1.43
125	0.444	1.45
175	0.440	1.41
212	0.441	1.41
265	0.443	1.43
285	0.443	1.42
300	0.440	1.45
325	0.444	1.41
345	0.444	1.43
Mean	0.442 ± 0.0004	1.43 ± 0.0045

Wood's Alloy.

Temp.	ν_θ.	κ_θ.
100° C.	0.397	1.80
125	0.400	1.78
150	0.395	1.76
175	0.396	1.77
200	0.398	1.76
220	0.399	1.80
242	0.395	1.78
265	0.397	1.79
285	0.396	1.79
305	0.398	1.78
325	0.395	1.76
345	0.399	1.76
365	0.400	1.80
385	0.397	1.76
407	0.397	1.78
425	0.398	1.77
450	0.395	1.77
465	0.398	1.78
480	0.397	1.76
Mean	0.397 ± 0.00045	1.78 ± 0.0047

Discussion of Results.

From the results, it is obvious that within the limits of the investigation and the sensitivity of the apparatus used, the optical properties of the metals investigated are constant.

Since the optical properties of Sn, Pb, and Bi are constant and the factors for Wood's Alloy are constant, and Wood's Alloy is made of Sn, Pb, Bi, and Cd, it seems reasonable to conclude that the optical properties of cadmium are constant.

With the view of possibly making a comparison between the factors of the molten and the solid state some observations were made on a highly oxidizable metal (copper). It was found that the age of the surface after polishing as well as the kind of abrasive used in making the mirror greatly affected the results so that no consistent data could be obtained. From this it was concluded that it would be necessary to prepare the mirror in a reducing atmosphere and without the use of an abrasive if accurate results are to be obtained. To prepare a surface under these conditions seems practically impossible. This condition prevented any comparison of the data for the two states. This difficulty applies only to soft, low melting point, highly oxidizable metals and the other metals could not be investigated because their melting points are above 500 degrees C. This point is the upper limit of the work as was previously stated.

PROBABLE ERROR.

The least squares solutions of the experimental results show that the probable error of these quantities is under one half of one per cent. The probable error of the adjustment of the polarizing and analyzing prisms with respect to their circles was well under one-half of one per cent. It seems therefore probable that the final values of these constants are not in error by more than one per cent.

THEORETICAL.

Drude's equations[1] for the optical constants of metals are:

$$\nu^2(1-\kappa^2) = 1 + \sum \frac{\Phi'}{1-\left(\frac{\tau_h}{\tau}\right)^2} - 4\pi \sum \frac{m'N}{r^2+\left(\frac{m'}{\tau}\right)^2} \qquad (8)$$

$$2\nu^2\kappa = 4\pi\tau \sum \frac{Nr}{r^2+\left(\frac{m'}{\tau}\right)^2}, \qquad (9)$$

where τ_h = natural period of the electrons of class h.
τ = natural period of the incident light.
N = number of electrons per cubic centimeter.
$m' : me$ m = inert mass of the electron.
e = charge on an electron.
$r = \frac{N}{\sigma}$ σ = electrical conductivity.
Φ' = proportional to the displacement of the electrons from their positions due to the influence of a constant force. For conducting electrons Φ' is ∞.

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[1] Drude, Theory of Optics, translation by Mann, p. 398.

The experimental work shows that ν_θ and K_θ are constant. Indicating all the constant terms in equations (8) and (9) as such, they become:

$$C = 1 + \sum \frac{\Phi'}{1 - \left(\frac{\tau_h}{\tau}\right)^2} - E \sum \frac{F}{\frac{N}{\sigma^2} + \frac{1}{N} G^2} \tag{10}$$

$$H = J \sum \frac{1}{\frac{1}{\sigma} + \frac{\sigma}{N^2} P} \tag{11}$$

where C, E, F, G, H, J and P are constants. If equation (11) is true then:

$$\left| \frac{1}{\sigma} + \frac{\sigma P}{N^2} \right|_{t_1} = \left| \frac{1}{\sigma} + \frac{\sigma P}{N^2} \right|_{t_2}. \tag{12}$$

Since σ and N vary with the temperature, this identity must hold for all corresponding pairs of values of σ and N. To test this identity, data for mercury will be substituted.

For 0° C. $1/\sigma = 94 \times 10^{-6}$,
350° C. $1/\sigma = 135.5 \times 10^{-6}$,

N varies inversely as the expansion of the metal.

For 350° C. Let $N = 1$.
0° C. $N = 1.064$.

Substituting in equation (12), neglecting the first term on each side of the equation (this is possible because of their size in comparison with the following terms) and inverting, the result is:

$$106 = 135,$$

which is obviously not true, the difference being about 21.5 per cent. Since this difference is far greater than the experimental error of the work, the validity of equation 11 seems doubtful. As to equation 10 very little can be said as no data is available as to the variation of Φ' and τ_h with the temperature.

In conclusion, I wish to thank Professors Hall and Minor and all others whose kind assistance made this work possible.

Physical Laboratory,
University of California,
April, 1922.

BOMBARDMENT OF METAL SURFACES BY SLOW-MOVING ELECTRONS.

By H. E. Farnsworth.

Synopsis.

Secondary Electrons Produced by Electronic Bombardment of Nickel.—The main features of the apparatus used are: an equi-potential nitrate-coated Pt cathode heated by radiation from a tungsten spiral filament; a series of insulated diaphragms to limit the beam of primary rays and for use in determining their velocity; and a long Faraday cylinder in front of which the nickel target could be alternately interposed and withdrawn. By baking out the tube and using liquid air traps an extremely low vacuum corresponding to less than 10^{-7} mm. was attained. The secondary current was determined from the difference between the current to the Faraday cylinder and that to the interposed target. (1) *Ratio of the secondary (emergent) to the primary (incident) electron current* was found to be independent of the roughness of the surface, but to vary with the treatment. After heating the target red-hot by high frequency induction for some minutes, a limiting curve was reached which probably represents the characteristics of *nickel itself, free from surface contamination.* In this case the secondary electrons begin when the primary velocity is as low as 0.2 volt; the ratio to primary current then increases rapidly with primary velocity to about 4 volts, remains constant to about 9 volts, then again increases reaching a value of unity for a primary velocity corresponding to about 260 volts. *The effect of exposure to air or hydrogen* is to increase very considerably the secondary current and to round out the flat part of the curve between 4 and 9 volts. (2) *Velocity distribution curves of the secondary electrons* indicate that for primary electrons of less than 9 volts velocity, most of the secondary electrons have velocities nearly equal to the primary velocity, while for primary velocities above 9 volts, the percentage of secondary electrons having small velocities increases with the primary velocity, although a small proportion have velocities nearly equal to the primary velocity up to at least 110 volts.

Reflection and Emission of Electrons from a Nickel Surface Bombarded with Electrons of Velocity 0 to 260 Volts.—It is suggested by the above results, that reflection occurs for all the primary velocities investigated, and that emission or ionization begins at about 9 volts and increases with the primary velocity.

Contact difference of potential between a gas-free nickel surface and an ordinary baked nickel surface was found to be 0.8 volt.

Method of making a gas-tight glass joint for high vacuum work by soldering with Wood's metal, the platinized and copper-coated surfaces of a ground joint, is described.

Introduction.

STUDIES of the secondary electrons produced by electronic bombardment of metal surfaces have previously been made by various experimenters. However, the fact that most of the results were obtained previous to the development of modern high-vacuum technique combined with the failure of the small amount of recent work to agree with these older results, leaves the important questions of this problem still unanswered. It is well known that the number of secondary electrons depends upon the velocity of the incident or primary beam, that more electrons leave the surface than strike it if the primary velocity is great enough, but the following characteristics of various metals are still not definitely determined: (1) the magnitude of the secondary electron current as a function of the primary velocity; (2) the velocity distribution of the secondary electrons for any given primary velocity.

Some of the earlier experiments carried out by Gehrts,[1] von Baeyer,[2] and Campbell [3] indicate that the above characteristics are the same for all metals tried, platinum, copper, nickel, aluminum, lead and cobalt. Secondary electrons were found when using a primary velocity as low as one volt. The number of secondary electrons increased with increase of the primary velocity up to about 5 volts. With further increase of primary velocity to about 11 volts, the secondary current decreased. Beyond 11 volts it increased rapidly to a maximum at about 200 volts and then decreased gradually and continuously. Above about 30 volts primary velocity more electrons were found to leave the surface than strike it. Most of the secondary electrons apparently had velocities less than 10 volts while none were found with velocities greater than 30 volts even when the primary velocity considerably exceeded 30 volts.

A. W. Hull,[4] working more recently with copper, obtained a slight minimum in his secondary electron curve, but it comes at 5 volts instead of at 11 volts, with a slight maximum at 2.6 volts. He found the ratio of the secondary electron current to the primary, for any given primary velocity, to be much smaller than that of the previous experimenters, being only about 40 per cent. at 50 volts primary velocity. I. G. Barber,[5] also working recently with copper, concluded that there were no secondary electrons when the primary velocity was less than about 10 volts. F. Horton and Miss A. C. Davies[6] found secondary electrons from platinum when the primary velocity was as low as 3 volts. They found no secondary electrons with velocities greater than 10 volts when using a primary velocity of 70 volts. They did not heat the platinum above 300° C. Davisson and Kunsman,[7] working with nickel, found some secondary electrons with velocities nearly equal to that of the primary beam. They did not investigate the number of secondary electrons as a function of the primary velocity.

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[1] Gehrts, Ann. d. Phys., *36*, p. 995, 1911.

[2] O. von Baeyer, Phys. Zeitschr., *10*, p. 176, 1909; Deutsch. Phys. Gesell., Verh., *10*, 24, p. 953, 1908; Ber. d. D. Phys. Ges., *10*, p. 96 and p. 953, 1910.

[3] N. R. Campbell, Phil. Mag., *22*, p. 276, 1911; *24*, p. 527, 1912; *25*, p. 803, 1913; *28*, p. 286, 1914; *29*, p. 369, 1915.

[4] A. W. Hull, Phys. Rev., *7*, p. 1, 1916.

[5] I. G. Barber, Phys. Rev., *17*, p. 322, 1921.

[6] F. Horton and Miss A. C. Davies, Royal Soc. Proc., *97A*, p. 23, 1920.

[7] Davisson and Kunsman, Science, *54*, p. 522, 1921.

The object of the present investigation is to obtain the characteristics of various metals which have been freed from gas under the best vacuum conditions available, and to see how these characteristics vary with the metal and the roughness of the surface. Up to the present only nickel has been studied in detail.

APPARATUS.

An apparatus suitable for the carrying out of this investigation must be so constructed that the following conditions may be realized: (1) a primary electron stream of uniform velocity and cross-section; (2) an accurate means of measuring the total primary current; (3) an accurate means of measuring the secondary electron current; (4) means of measuring velocities of both primary and secondary electrons.

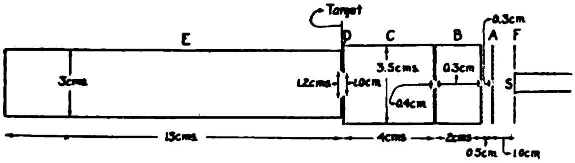

Fig. 1.

The final form of apparatus used is shown in cross-section in Fig. 1. Condition (1) is satisfied by accelerating the primary electrons to the diaphragm, *A*, from an equipotential source, *S*. Some of these electrons shoot through the hole in *A*, through *B* and *C* into *E*. The primary beam is thus limited in cross-section by the various sharp-edged diaphragms along the path. *F* is a focusing plate concentric with *S*. The electron stream is kept from scattering by means of a magnetic field in the direction of the stream. Condition (2) is realized by the use of the long cylinder, *E*, which is practically a perfect absorber for the electrons that once get into it. (3) By means of a magnetic control[1] a nickel target can be moved over the hole in the end of *E*, into the path of the electron stream. The secondary electrons which leave the target are received by the cylinder *C*. The insulated diaphragm *D* makes it possible to determine whether the presence of the target causes any scattering of the primary beam. (4) The velocity distribution of the primary electrons can be obtained by putting a variable retarding potential on *D* and *E* and measuring the total current as a function of the potential in the usual way. Similarly, the velocity distribution of the secondary electrons may be obtained by varying the potential of *C* and *D*. The apparatus was constructed entirely of nickel, glass and quartz except for the nitrate-coated platinum source of electrons. A quartz tube, supports the platinum source which is coated with barium, strontium, and calcium nitrates to increase the emission of electrons. The heat for the source is furnished by an electric current which passes through a plane tungsten spiral, placed inside the quartz tube and very close to but not in contact with the platinum foil. With this arrangement the source is always an equipotential one which permits an accurate measurement of its potential. A larger primary current was obtained when fine nickel gauze was placed over the openings in *A* and *B*, as indicated in Fig. 1 by the dotted lines. This is probably because there is less distortion of the field at the openings when the gauze is used. The cylinders *B*, *C*, and *E* were lined with fine nickel gauze so as to decrease any possible multiple reflection of electrons. The whole apparatus was cleaned with distilled ether after assembling to remove any grease that might be present. The apparatus was enclosed in a glass tube which, after being evacuated, was heated by an electric furnace to 400° C. for several hours with the pumps working continuously. Liquid air was kept on the condensing trap continually during the time that the tube was connected to the vacuum line, so that oil and mercury vapors were never allowed to enter the tube. The pumps were kept going during the observations so that the results were obtained under extremely good vacuum conditions. A pressure of 10^{-6} mm. Hg could be observed on the McLeod gauge used and while the observations were taken the mercury stuck to the top of the gauge, a negative pressure of 2 cm. of Hg being necessary to release it, so that the gas pressure in the tube must have been much less than 10^{-7} mm. Hg. Observations as well as calculation show that ionization of the residual gas at this pressure is negligible since practically no current to *C* and *D*, Fig. 1, was observed when primary electrons were driven into *E*.

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[1] The magnetic control was placed to the left of the cylinder, *E*, as far away from the source as possible, to avoid changing the state of magnetization of that part of the apparatus which limits the electron stream.

In order to facilitate adjustment and to prevent the waste of time necessitated by cutting open the tube containing the apparatus, a ground glass joint, having the same diameter as the tube (2 inches), was sealed on one end. To make the joint air tight and to avoid the presence of wax vapor, the joint was copper plated and soldered together with Wood's metal. The glass was first platinized by painting on a solution of platinum chloride and dextrine, then heated in an electric furnace until the platinum was reduced to the metallic form. Four or five separate coats and heatings were necessary to make the platinum sufficiently conducting so that a uniform deposit of electrolytic copper could be obtained. At first difficulty was experienced in obtaining a deposit of copper which did not let air through between the copper and platinum. This was finally overcome by taking special precautions in the cleanliness of the solution of copper sulphate used, and by the addition of a small amount of glucose to the solution, which produced a finer grained deposit. The copper was deposited on the two parts of the joint so that when they were fitted together the copper plating completely covered the outside of the joint. Wood's metal was used to solder the two parts together because of its low melting point. With zinc chloride it required very little heating to coat the surface of the copper with the alloy. The vapor pressure of Wood's metal is not exactly known, but it should cause no trouble in the tube since two inches of tight-fitting ground-glass joint intervene to make the rate of diffusion extremely small. The ground joint was placed near one end of the tube and far enough from the metal parts so that it was possible to bake out the apparatus without heating up the joint. The inner seal which was attached to the removable part of the ground joint supported the wires carrying the heating current and the quartz tube, and also two small glass tubes, one of which held the focusing plate, *F*, and the other the diaphragm, *A*.

METHOD OF PROCEDURE.

Since the magnitude of the primary current was found to vary with the velocity of the primary electrons, the ratio of the secondary current to the primary current was measured as a function of the primary velocity. The secondary current was obtained by taking the difference between the total primary current to *E* when open, and the current to the target when it was over the hole in the end of *E*. Direct measurement of the secondary electron current to the cylinder, *C*, gave the same result as the above method. *B*, *C*, *D*, and *E* were all grounded during this measurement so that the number and energy of the secondary electrons were not affected by an external field. In order to obtain larger primary currents for the small velocities a retarding field was placed between *A* and *B*, so that the primary electrons were first accelerated to *A*, retarded to *B*, and then passed on into *E* with a velocity measured by the difference between the accelerating and retarding potentials. The procedure was then to measure the primary and secondary electron current for various primary velocities, obtained by varying the potential of *S*.

To determine the velocity distribution of the primary electrons, *i.e.*, to find out what fraction of the total number had a velocity corresponding to the net accelerating voltage, a varying retarding potential was put on E and D, with E open, the potential of the two being the same. This potential was varied in steps from zero up to the accelerating voltage, and the corresponding currents to the cylinder, E, measured. By trial, it was found that no electrons hit D. The velocity distribution of the secondary electrons for any given primary velocity was obtained by measuring the current to the target as the potential of B, C, and D (all being the same) was varied in steps from zero up to the voltage corresponding to the primary velocity. B was kept at the same potential as C and D, for it was found that the primary stream was scattered if there was an appreciable potential gradient between B and C. This procedure is based on the assumption, which seems to be a reasonable one, that the velocity of impact of the primary electrons is given by the potential drop from the target to the source, independent of the potentials of B, C, and D. Changes in the potential of B, C, and D produce changes in the magnitude of the primary electron stream, but these are taken account of, since the total current to E, as well as the current to the target, was measured each time that the potential of B, C, and D was changed. The ratio of the secondary electron current to the total current received by E as a function of the retarding potential on B, C, and D then gave a measure of the velocity distribution of the secondary electrons, since the secondary electrons which leave the target must have a velocity greater than that corresponding to the retarding field which tends to keep them on the target.[1]

RESULTS.

As shown by the curves of Fig. 2, the ratio of the secondary to the primary current as a function of the velocity was obtained for the following: (1) a polished nickel target; (2) a nickel target which had been cleaned with fine emery paper; (3) nickel target etched with acid; (4) nickel target covered with fine nickel gauze; (5) a copper target; (6) a polished nickel target after prolonged heat treatment at bright red heat. The first five curves were obtained with targets which had received the same heat treatment as the rest of the apparatus, *i.e.*, baked at 400° C. for several hours. The results show that the number of secondary electrons is independent of the roughness of the surface, but that covering the surface with fine nickel gauze considerably reduces the number of secondary electrons. The secondary electron current from a copper target seems to be greater than that from a nickel target. However, since the above observations were taken before sufficient heating to eliminate the effects of occluded gas, no final conclusion can be drawn as to the difference in the secondary electron current from copper and nickel.[1]

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[1] The above method assumes, of course, that the retarding potential on the cylinder, C, is a measure of the total velocity, and not of components perpendicular to the surface of the cylinder. This would only be true if a small target was placed at the center of a hollow spherical conductor large compared to the size of the target. However, the error introduced by an apparatus having the dimensions of Fig. 1 should not be serious. In any case, it would be constant and such as to make the value obtained for the velocity smaller than the true value, so the fact that large values were obtained for at least some of the secondary electrons would not be altered.

Prolonged heating of the nickel target at bright red heat was accomplished by high-frequency induction. The target could be moved up into a bulge in the tube so that only the target was heated to red heat when the tube was surrounded by a few turns of wire which carried the high-frequency current. The appearance of the target was unchanged by the heat treatment, although a considerable amount of nickel was evaporated onto the walls of the glass tube opposite the target. Since the pumps were kept going during this heat treatment the gas pressure remained small at all times (less than .00001 mm. Hg), and when the heating had been continued until the limiting curve was obtained the gas pressure even during the heating was so low that the mercury stuck to the top of the McLeod gauge.

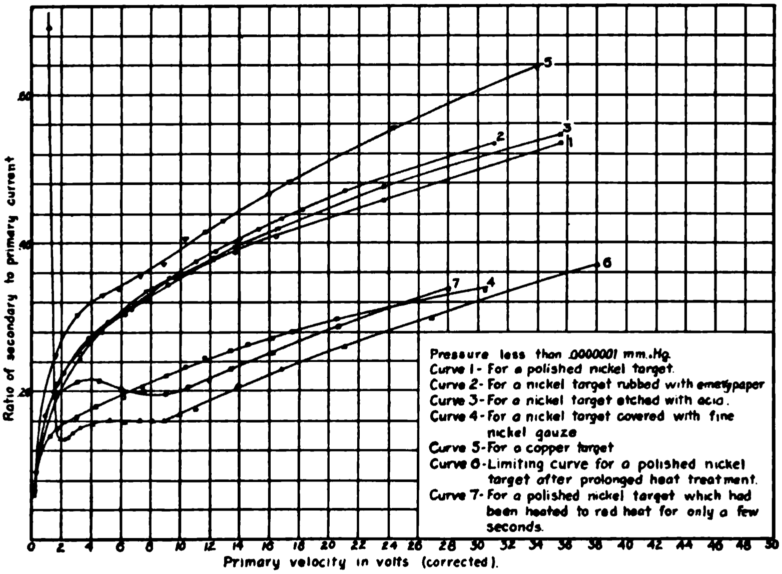

Fig. 2.

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[1] It is interesting to note that a curve of the same form as curve 1 was obtained with a preliminary form of apparatus, in which the nickel target was moved along the axis of the tube, similar to the arrangement used by A. W. Hull.

As shown by curve 6, the prolonged heat treatment reduces the secondary electron current considerably and changes the general shape of the curve. Curve 7 was obtained after the target had been heated to bright red heat for only a few seconds (about 10). Further heating gradually changed and lowered the curve from the form 7 to the form 6. Curve 6 seems to be the limiting value since additional heating produced no further change. To make sure that the change produced was due to elimination of gas and not to a change in the structure of the metal, the apparatus was exposed to air and then evacuated and baked at 400° C., after which the original curve 1 was obtained. Curve 6 was then repeated after prolonged heating. Exposing the apparatus to hydrogen at a pressure of 2 cm. Hg for several days increased the secondary electron current as shown by curve 10, Fig. 3, but again heating the target at bright red heat reduced this current to the same limiting values which it reached after heating subsequent to the exposure to air, so that it seems safe to conclude that the final curve is one which represents the true characteristics of the metal.

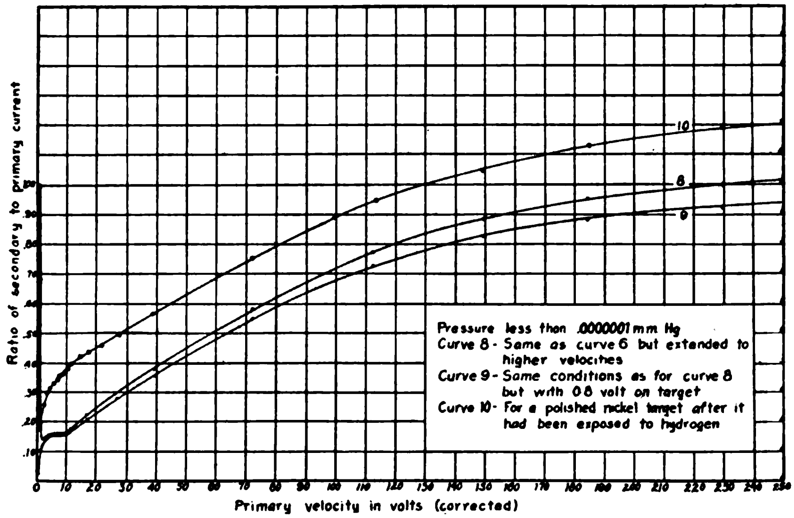

Fig. 3.

As already seen from curve 7, an enormous change in the curve was produced by only a few seconds heating of the target at bright red heat, and practically the whole change produced by the continued heating at this temperature was found to take place during the first few minutes. The curve obtained after 30 min. of this heating was only slightly higher than that obtained after one hour of heating. Further heating produced no noticeable change in the curve, *i.e.*, the limiting form was reached after about one hour of heating at bright red heat. Only about 20 min. of this heating seemed to be necessary to obtain the limiting curve subsequent to the exposure of the apparatus to hydrogen under the conditions previously stated. The heating at red heat was not effected continuously, but at about one-minute intervals for periods of one minute, so as to prevent overheating of the glass tube. No results for a copper target after continued heating have been obtained as yet, due to experimental difficulties.

After the target had been heated to red heat it assumed a negative potential of about 0.8 volt with respect to the surroundings, thus producing the sharp rise at the low-velocity end of the curves obtained after heating. By neutralizing this negative potential with a positive potential of 0.8 volt, curve 9 was obtained. It will be noticed that this curve lies below curve 8, the difference between the two curves increasing with the primary velocity. This, however, is easily explained if we consider that before the contact potential is neutralized the secondary electrons are pulled off the target by a potential difference of 0.8 volt which causes more electrons to leave the target than would if no field existed. This difference would naturally increase with increase in the number of secondary electrons. Curve 9 can then be considered as representing the true secondary electron characteristics of nickel produced in an equipotential region. The curve obtained after allowing the apparatus to stand over night, during which time the pressure remained less than .00001 mm., was found to be somewhat higher than the limiting form, *i.e.*, the secondary electron current had increased slightly. The contact potential of the target had also slightly decreased. This result is probably due to absorption of gas and to gas diffusing out from the interior of the target.

A typical set of data, taken after prolonged heat treatment, is shown in Table I. Column 1 shows the retarding potentials used between *A* and *B*, Fig. 1. These retarding potentials gave the best velocity distribution of the primary electrons, although no difference could be noticed in the curve obtained with a constant retarding potential of 20 volts. Column 2 contains the primary velocity in volts (uncorrected). The total current was measured before and after the current to the target was observed and the average taken as indicated in Column 3. Column 5 contains the current to the diaphragm, *D*, when the cylinder *E* was open and when it was closed by the target. As stated in the description of apparatus, these observations show whether the presence of the target causes any scattering of the primary beam which would result in an

Table I.

1	2	3			4	5 (5, a)	(5, b)	6	7
		Total Current.				Current to *D*.			
Retarding Potential between *A* and *B*.	Velocity in Volts (Uncorrected).	First.	Last.	Average.	Current to Polished Target.	With Target over Hole in *E*.	With *E* Open.	Col. 3–Col. 4.	Ratio of Secondary to Primary Current.
3.0	1.0	62.0	62.0	62.0	0.0	0.0	0.0	62.0	1.000
3.0	1.5	162.5	161.5	162.0	1.0	0.0	0.0	161.0	0.994
3.0	1.8	187.5	187.5	187.5	11.5	0.0	0.0	176.0	0.938
3.0	2.0	215.0	222.0	218.5	71.0	0.0	0.0	147.5	0.675
3.0	2.3	234.0	237.0	235.5	193.0	0.0	0.0	42.5	0.181
3.0	2.5	227.0	229.0	228.0	194.0	0.0	0.0	34.0	0.149
3.0	2.7	208.5	208.0	208.2	180.0	0.0	0.0	28.2	0.135
3.0	3.0	218.0	217.0	217.5	188.0	0.0	0.0	29.5	0.136
3.0	3.2	233.0	235.0	234.0	202.0	0.0	0.0	32.0	0.137
3.0	3.5	231.0	233.0	232.0	198.5	0.0	0.0	33.5	0.144
3.0	4.0	232.0	234.0	233.0	197.8	0.5	0.0	35.2	0.151
4.5	5.0	216.0	217.0	216.5	183.8	1.2	0.2	32.7	0.151
6.0	6.0	238.0	238.0	238.0	200.0	1.5	0.3	38.0	0.160
6.0	7.0	225.3	228.0	226.6	191.0	2.0	0.3	35.6	0.157
7.5	8.0	237.0	239.0	238.0	200.0	2.0	0.2	38.0	0.160
7.5	9.0	247.0	247.0	247.0	208.0	2.6	0.2	39.0	0.158
9.0	10.0	235.0	234.0	234.5	197.0	3.0	1.0	37.5	0.160
10.5	11.0	236.0	238.0	237.0	197.0	3.2	1.0	40.0	0.169
10.5	12.0	239.0	235.0	237.0	196.0	5.0	1.2	41.0	0.173
10.5	14.8	222.8	222.2	222.5	176.5	5.8	1.2	46.0	0.206
10.5	17.7	241.0	240.6	240.8	186.0	5.8	1.2	54.8	0.228
20.0	22.0	243.0	242.0	242.5	180.0	6.0	1.0	62.5	0.258
20.0	27.2	219.0	218.0	218.5	153.5	6.5	0.7	65.0	0.298
20.0	40.0	235.5	235.5	235.5	147.0	7.5	0.8	88.5	0.376
20.0	72.5	236.0	236.0	236.0	100.0	14.5	0.5	136.0	0.576
20.0	113.0	239.0	243.0	241.0	56.0	19.8	0.7	185.0	0.768
20.0	150.0	248.0	243.0	245.5	29.5	22.5	1.0	216.0	0.880
20.0	185.0	226.0	226.0	226.0	12.0	27.8	2.0	214.0	0.947
20.0	230.0	212.0	213.0	212.5	1.0	27.0	1.5	211.5	0.995
20.0	260.0	233.0	228.0	230.5	−5.0	33.0	2.8	235.5	1.020

apparent secondary electron current. The observations show that practically no primary electrons hit *D*, but nearly all went through the hole into *E*, when *E* was open. The current to *D* was somewhat larger when the target was over the hole in *E*. It was, however, much too small to account for the apparent secondary electron current by a scattering of the primary beam. From Column 5*a*, Table I., we see that there was no current to *D* until a primary velocity of 4 volts (uncorrected) was reached, after which the ratio of this current to the total secondary current (obtained by taking the ratio of the corresponding values of Column 5*a* and Column 6) increased to about 0.12 at 15 volts primary velocity and then remained more or less constant until 150 volts primary velocity was reached, after which it again increased to about .14 at 260 volts. The magnitude of this current is easily explained if we consider that, of the secondary electrons which leave the target in random directions,[1] a small percentage will be intercepted by *D*, for, although *D* was as close as practicable to the target (something less than one mm.), it subtended an angle sufficient to account for the current which it received.[2] Column 7 was obtained, as previously explained, by dividing the difference between the total current and the current to the target by the total current. Since only the ratio of the currents was desired no attention was paid to their absolute magnitudes. The currents for velocities of the order of a volt and less were easily measured with a D'Arsonval galvanometer of sensibility 10^{-10} amps. per mm. of deflection and much larger currents were obtained for the higher velocities.

The velocity distributions of the primary electrons, obtained as previously explained, are shown in Figs. 4 to 6. The dotted curves in

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[1] John T. Tate, PHYS. REV., *17*, p. 394, 1921. C. Davisson and C. H. Kunsman, Science, *54*, p. 522, 1921.

[2] In this case we should expect that the ratio of the current to *D* to the total secondary current would remain constant, independent of the magnitude of the secondary current. The increase of this ratio for the lower primary velocities may be due to the effect of the magnetic field, causing the bulk of the secondary electrons, having sufficiently low velocities, to leave the target in the direction of the field, *i.e.*, along the axis of the tube and thus preventing them from striking *D*. Then, only those secondary electrons which have a velocity sufficient to overcome the effect of the magnetic field would be able to reach *D*. The ratio of this number to the secondary current would obviously increase with the primary velocity until the bulk of the secondary electrons had a velocity great enough to be unaffected by the magnetic field (see velocity distribution curves of secondary electrons below). The increase of current to *D* which begins at the higher velocities may be the result of reflection of the secondary electrons from the inner surface of the cylinder, *C*, back to *D*. Although this reflection is decreased by the presence of gauze on the surface, as previously seen, the velocity distribution curves of secondary electrons, shown below, indicate that there are some high-velocity secondary electrons leaving the target which might produce an appreciable effect due to their reflection from the cylinder *C* back to the diaphragm *D*. Some of these reflected secondary electrons would also strike the target and thus introduce an error since it has been assumed, for the results obtained, that the only electrons hitting the target are primary electrons. This effect, however, would not be noticeable until comparatively large values of the primary velocity had been reached. A rough calculation shows that, for a primary velocity of 30 volts, less than 0.3 per cent. of the incident electrons on the target are secondary electrons from the cylinder *C*. At 100 volts it amounts to less than 1.0 per cent. This error would cause the observed secondary electron curve to lie below the correct curve. In this calculation it was assumed that, due to the effect of the magnetic field, all of the secondary electrons from the target left in directions so as to hit the opposite end of the cylinder *C*, instead of leaving in random directions, and a similar assumption was made for those leaving the end of the cylinder *C*.

Fig. 4 were obtained by plotting the slopes of the original curves as ordinates. The ordinate at any point is then proportional to the number of electrons having a velocity corresponding to the retarding potential.

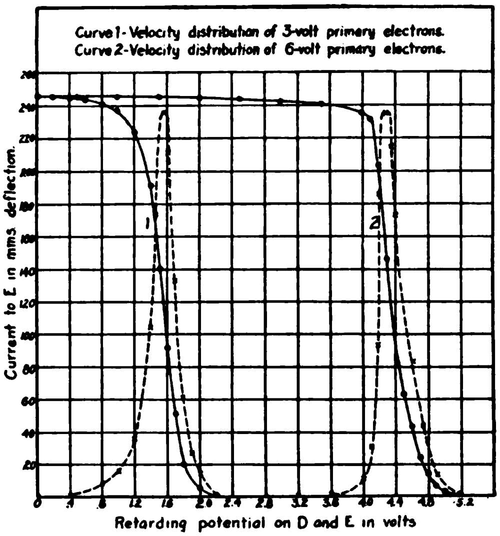

Fig. 4.

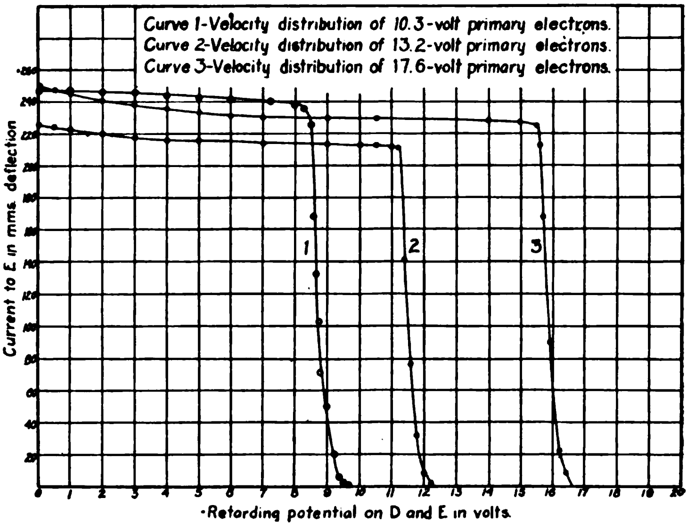

Fig. 5.

It will be noticed that, although the velocity distribution is probably as good as could be expected, the bulk of the electrons have velocities somewhat lower than that corresponding to the net accelerating voltage applied. This must be due to a contact potential between the platinum source and the nickel. Because of this difference the velocities as given in Column 2 of Table I. must be corrected. This correction, which varies slightly with the primary velocity, was made before the curves were plotted so that the abscissa of the curves in Figs. 2 and 3 are the corrected velocities. Since the velocity distribution curves show that the velocities vary over a range of about one volt, the mean value was taken as the correct one. It was found that the velocity distribution of the primary beam depended to a slight extent on the potential of the focus plate, F, the best distribution being obtained with the potential

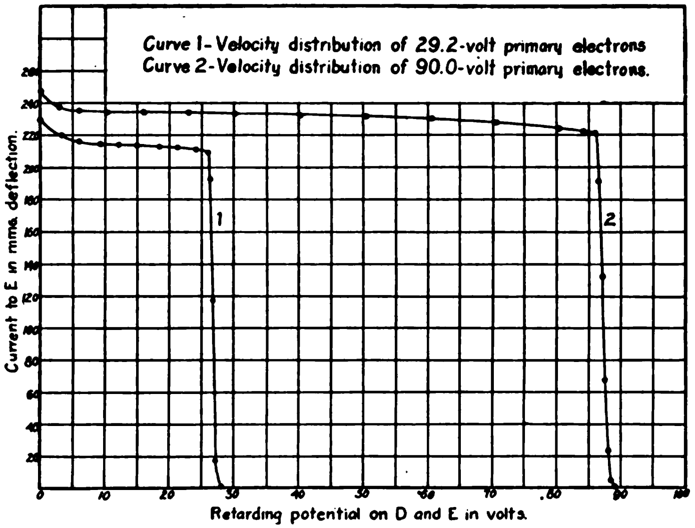

Fig. 6.

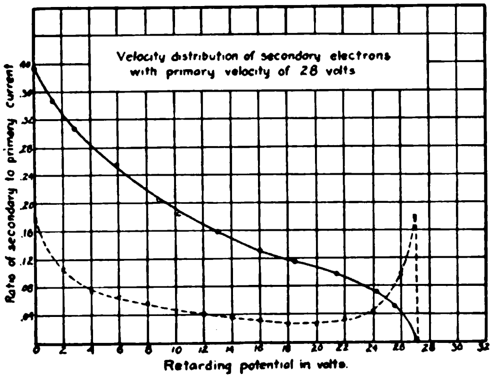

Fig. 7.

of *F* the same as that of the source, *S*. For this reason *S* and *F* were kept at the same potential during all the observations although there were other potentials of *F* which gave larger primary currents.

The velocity distributions of the secondary electrons, obtained as explained under "procedure," are shown in Figs. 7 to 9. The dotted curves were obtained by plotting the slopes of the other curves as ordinates. These curves indicate that, when the primary velocity is below about 9 volts, a large percentage of the secondary electrons have velocities nearly equal to the primary velocity and a very small percentage have velocities less than one volt. For higher primary velocities the distribution changes, there being many secondary electrons having low velocities. The percentage of secondary electrons having velocities less than 5 volts, say, increases as the primary velocity increases. There are, however, a few per cent. having velocities nearly equal to that of the primary electrons when the primary velocity is as great as 110 volts. As stated in the introduction, Gehrts and von Baeyer found no secondary electrons with velocities greater than 30 volts. The present results, however, agree qualitatively with those of Davisson and Kunsman, who found

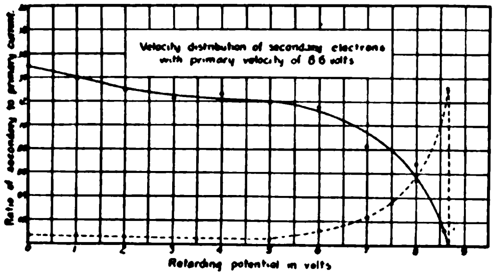

Fig. 8.

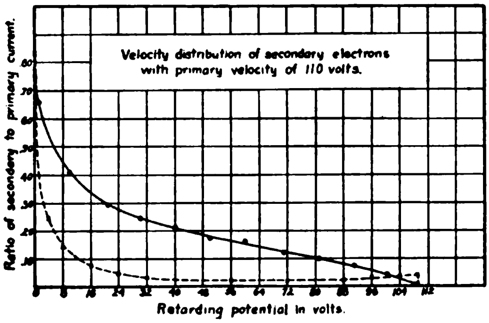

Fig. 9.

some secondary electrons with velocities nearly equal to that of the primary stream.

DISCUSSION OF RESULTS.

In the preceding discussion the use of the words "reflection" and "emission" has purposely been avoided, since there has been some difference of opinion as to whether actual reflection of the primary electrons occurs or whether all of the secondary electrons are produced by ionization at the metal surface. It is certain that emission occurs at high velocities where more electrons leave the surface than strike it, but the question is obviously, whether reflection occurs at all, and if so, at what velocity of impact emission begins. Gehrts and von Baeyer concluded from the nature of their results (see introduction) that reflection occurred only below 11 volts, and that at this velocity an emission began which increased rapidly with the primary velocity. They were, however, unable to interpret the maximum in the secondary electron curve at 5 volts. They considered that their explanation would have seemed more plausible if the number of secondary electrons had decreased steadily with the primary voltage up to 11 volts and then increased, instead of showing a maximum at about 5 volts. The phenomena could then have been considered as due to reflection which was large for small primary velocities but which decreased with increasing velocity to 11 volts, where an emission began and increased rapidly with further increase in primary velocity. The results of the present investigation show that the maximum which they observed at 5 volts was probably due to the effects of absorbed gas, since it disappears with continued heating. Since I. G. Barber obtained no secondary electrons below about 10 volts' primary velocity he concluded that there is no such thing as reflection of electrons and that emission begins at about 10 volts.

The following features of the present investigation show that a new factor enters into the production of secondary electrons from nickel at about 9 volts: (1) the sudden change in slope of the secondary electron curve (Figs. 2 and 3) at about 9 volts; (2) the difference between the velocity distribution of secondary electrons when the primary velocity is 8.6 volts or less, and that when the primary velocity is considerably greater than this. These results lead one to the interpretation that reflection of electrons from nickel occurs for all the primary velocities investigated, the reflection increasing between 0 and 4 volts' primary velocity and then remaining constant to 9 volts, where emission begins and increases with increase of primary velocity to at least 260 volts. That there are some high-velocity electrons present, when the primary velocity is as great as 110 volts, indicates that reflection continues after emission begins, so that above 9 volts there is both reflection and emission. According to this idea the reflected electrons may be considered to have velocities nearly equal to the primary velocity, *i.e.*, reflection involves a change in direction without much loss in energy, while the emitted electrons have a much smaller velocity.

The above interpretation is further substantiated by a phenomenon which was observed when obtaining the velocity distribution of the primary electrons. It will be noticed, from the velocity distribution curves of the primary electrons, that when the primary velocity was less than 9 volts, all of the primary electrons had velocities nearly equal to that corresponding to the applied voltage. For larger primary velocities, however, there are some low velocity electrons present, as indicated by the rise of the left end of the curves. Also, the number present appears to increase with the primary velocity. This can be explained, with the previous interpretation, as being due to emission of electrons from the edges of the diaphragms which limit the primary beam. Thus, since below 9 volts no emission occurs, there are no low-velocity electrons present in the primary beam.

The accuracy in determining the ionization potential depends, of course, on the velocity distribution of the primary beam. Since the velocity varies over a range of about one volt, the mean velocity was taken as the correct one, as previously mentioned. If, however, the electrons with the highest velocity are sufficient in number to produce an appreciable effect, an error will be introduced equal to the difference between this higher velocity and the mean value. Hence the value obtained may be subject to a small correction.

Since the number of secondary electrons obtained at the low velocities was much greater before the continued heating than after, one must conclude that the reflection of electrons from the atoms of gas on a metal surface is greater than from the metal freed from gas. Since the ionization potential of hydrogen is about 11 volts, the increased secondary current below this velocity, as shown in curve 10, Fig. 3, is probably due to reflection from hydrogen atoms in the surface rather than ionization of them. The fact that curve 10 lies above the limiting curve for all velocities up to 260 volts also shows that more electrons are knocked out of the hydrogen atoms than from the nickel atoms. This is also true for air.

The method used is particularly well adapted to the extension of the investigation to other metals. Targets of the various metals can be inserted and the characteristics of each studied under the same conditions by moving them successively into the path of the primary electron stream. There is no reason to believe that the secondary electron characteristics should be the same for all metals, and a knowledge of their characteristics in this respect should be of value in connection with the electron theory of metals.

SUMMARY AND CONCLUSION.

1. The secondary electron characteristics of nickel, for low primary velocities, have been investigated in detail. The results are independent of the particular target used and also of the roughness of the surface.

2. Heating the nickel target to bright red heat in vacuo changed the shape of the secondary electron curve (Figs. 2 and 3) and decreased the magnitude of the secondary electron current. Exposing the surface to hydrogen again increased the secondary electron current. The same limiting form of curve was obtained after prolonged heating of the target at bright red heat independently of whether it had previously been exposed to air or hydrogen.

3. A sudden change in slope of the secondary electron curve occurs at about 9 volts' primary velocity, which, together with a difference in the velocity distribution of the secondary electrons for primary velocities below and above 9 volts, suggests that emission or ionization at the surface begins at this voltage and increases with primary velocity, and that between 0 and 9 volts only reflection occurs. The presence of secondary electrons with velocities nearly equal to that of the primary beam for the higher velocities suggests that reflection continues after emission begins.

This problem was suggested by Professor Max Mason and was carried out under the direction of Professor C. E. Mendenhall. The author wishes to express his indebtedness to these gentlemen for many valuable suggestions and criticisms throughout the progress of the work.

THE UNIVERSITY OF WISCONSIN,
May, 1922.

NOTE ON THE SPECIFIC HEAT. OF TUNGSTEN.

By Paul F. Gaehr.

SYNOPSIS.

Determination of the Specific Heat of Tungsten.—Various possible sources of error are suggested which must be taken into account if the method recently described by Smith and Bigler is to give accurate and reliable results.

IN the March number of this magazine, page 268, there appeared the abstract of a paper by K. K. Smith and P. W. Bigler on the "Specific Heat of Tungsten." The method there described is a clever one, and deserves a wide application. However, a number of points were overlooked, and the omission of the precautions puts the results in doubt. These points were discussed in part by Worthing (August, 1918) and myself (November, 1918) in this magazine. The points in question will be given below.

1. If the entire filament is used, there is no knowledge about heat conduction from the filament to the leading-in wires. Unless this is known, one cannot say what proportion of the electrical energy supplied goes to the filament.

2. In my article, referred to above, it was shown that unless temperature fluctuations be kept down to about 10° C., then one cannot consider as negligible the second and higher order derivatives in the expansion of $f(T)$ into a Taylor's Series. It would therefore seem wise for Smith and Bigler to modify their method by superimposing a small alternating current on a direct current, and to make sure that the temperature fluctuations from the mean do not exceed about 5° C.

3. Not only does it appear that the specific heat varies linearly with the temperature, which ought to be taken account of in the equations, but also it would seem from both Worthing's work and my own that the specific heat appears to be different for increasing current than for decreasing current. This, no doubt, is due to the fact that the radiation from the filament is not simply expressible as $f(T)$, but that to this function should be added a further term involving the time rate of change of the temperature. An alternating current method takes no account of this.

4. Unless the wave form of the alternating current is a pure sine form, quite free from harmonics, there are serious complications.

5. The presence of the Pyrex cylinder, on which the filament is wound, complicates the case in quite the same way as the leading-in wires, even if not to the same extent.

6. The spiral form of the filament tends to raise the temperature of the filament, so that it is doubtful that Langmuir's data are applicable.

It would seem that the experiment could be repeated, involving the above suggestions (excepting perhaps the third), and further using Worthing's method of potential leads. If, also, the temperature of the filament is determined pyrometrically, the method should then be an excellent one.

Second Series November, 1922 Vol. XX., No. 5

THE

PHYSICAL REVIEW.

THE MOBILITIES OF ELECTRONS IN HYDROGEN.

By Leonard B. Loeb.

Synopsis.

Electron mobilities in pure hydrogen have been measured for pressures of 73 to 635 mm., using a modified alternating field method with fields up to 70 volts/cm. Undamped oscillation of 15,000 to 200,000 cycles were obtained from a vacuum tube oscillator and were measured with a precision wave-meter. By using a constant retarding potential of 6 volts the disturbing effect of ions of impurities was eliminated and curves without the usual feet were obtained. The mobility (reduced to a pressure of 76 cm.) is found to be best represented by the equation: $k = 2.74 \times 10^6 / [399 + (Vo/d)(760/p^{3/4}]$, where Vo/d is the critical field in volts per cm. and p is the pressure in mm. *Comparison with kinetic theory.* This equation is practically of the same form as that found by less accurate measurements for nitrogen and since it differs from Townsend's theoretical equation: $k = a/[b + (Vo/d)(760/p)]^{1/2}$, either the mean free path of the electron or its loss of energy at impact are probably functions of the velocity of the electron. When the electrical fields are small the mobility at atmospheric pressure comes out 68.6 *m*/sec. whereas the kinetic theory gives 130.6; hence the actual *mean free path* must be only about half that assumed by the theory.

In a recent paper[1] the writer showed that by applying the high-frequency oscillations of an audion oscillator to the Rutherford alternating current method of mobility measurement, it was possible to determine electron mobilities in pure N_2 whose values were much higher than any previously obtained. The investigations in N_2 have been extended to H_2 with a considerable improvement in the technique, and it is the purpose of this paper to report the progress made.

The technique of measurement was improved along the following lines:

1. By the use of a new oscillating circuit which gave undamped oscillations whose amplitude could be varied at will without changing their frequency.

2. By the elimination of the asymptotic feet of the mobility curves through the use of a small retarding field of constant value. This field acted by removing the ions formed through the attachment of electrons to molecules of impurities.

3. By the elimination of the disturbing effect due to a gradual con-

tamination of the gas by impurities. These impurities were presumably liberated from the walls of the containing vessel on standing. The effect of the impurities was avoided by introducing fresh gas into the chamber before each set of readings.

4. By the use of a precision wave meter accurately covering the whole range of frequencies worked with in place of the rough instrument first employed.

1. The new oscillating circuit employed is shown in Fig. 1. The primary oscillations were set up in the system $C_1L_1F_1G_1P_1$, where the frequency is once and for all determined by the inductance L_1 and the capacity C_1. The oscillators $F_1C_1P_1$ were two Western Electric Company "E" tubes acting in parallel. The filament current and the plate resistance were always kept constant. The secondary inductance L_2, closely coupled to L_1, took the oscillations from it and thus placed an oscillating potential difference of the frequency of that in the primary circuit between the filament F_2 and the grid G_2 of a secondary "E" tube oscillator, $F_2G_2P_2$. The steady electron current from F_2 to G_2 driven by 200 volts direct current was therefore periodically interrupted by the oscillations in the primary circuit. A series of unidirectional

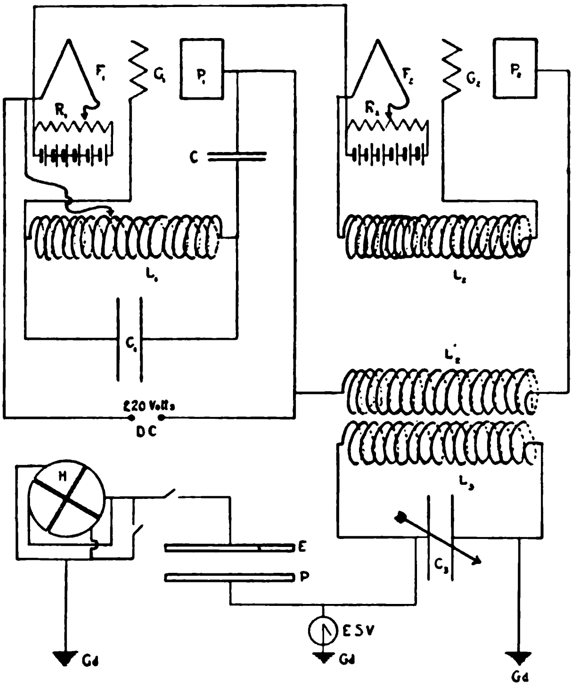

FIG. 1

current surges accordingly passed through the inductance L_2'. These acted on the inductance L_3 of the tertiary system L_3C_3 which was closely coupled to L_2'. Thus (when L_3C_3 was tuned to resonance with the primary system), there were set up across the condenser C_3 a continuous train of undamped oscillations. The inductance and capacity L_3 and C_3 were chosen to be as nearly the same as L_1 and C_1 as possible, the final sharp tuning being accomplished by a small variable air condenser in parallel with C_3. The amplitude of the oscillations in the system C_3L_3 was varied by varying the energy in the secondary circuit. This was accomplished by changing the secondary filament current through F_2 by varying R_2. One side of the condenser C_3 was grounded and the other side was connected to the plate source of electrons used in mobility measurement. The potential differences obtained across C_3 varied from 10 to 140 volts and were measured on two Kelvin electrostatic voltmeters. These were calibrated against a standard current voltmeter after each mobility determination. The frequencies used in these measurements varied from 15,000 to 200,000 cycles per second. To cover this range of frequencies and voltages it was necessary to use three sets of the inductances L_1, L_2, L_2' and L_3, each set having values of about 4×10^6, 1×10^6, and 3×10^5 cms. The capacities C_1 and C_3 were each a battery of 20 tin plates separated by glass, the capacity of which varied by about .0012 microfarad for each pair of tin plates.

2. In the previous paper[1] it was suggested that the asymptotic feet of the current-voltage curves obtained were caused by the formation of negative ions between the plates, due to the attachment of electrons to impurities present. These ions would not be removed by the high-frequency oscillations, and thus would build up a diffusion potential which would produce just such feet. In that paper the result of an attempt made to eliminate these by means of a small field of constant value which would pull the ions back to the lower plate was reported. The attempt failed in part because the fields used were too weak, and in part because of the fact that a portion of the feet were apparently due to instrumental irregularities of small magnitude in the ion chamber. In the present case two small flash-light cells giving a total potential difference of six volts were placed between the condenser C_3 and the lower plate P, so that the plate P was attached to the positive terminal of the cells. This arrangement was quite successful in eliminating the feet as may be seen in the curves of Fig. 2. In this figure the curves with crossed points represent the curves obtained without the cells, in hydrogen contaminated with about 1/3000 its volume of air. Such a contamination of the H_2 with air augmented the asymptotic feet very perceptibly. The curves

with the circled points are the mobility curves obtained under the same conditions with the cells inserted. It is seen that the curves obtained

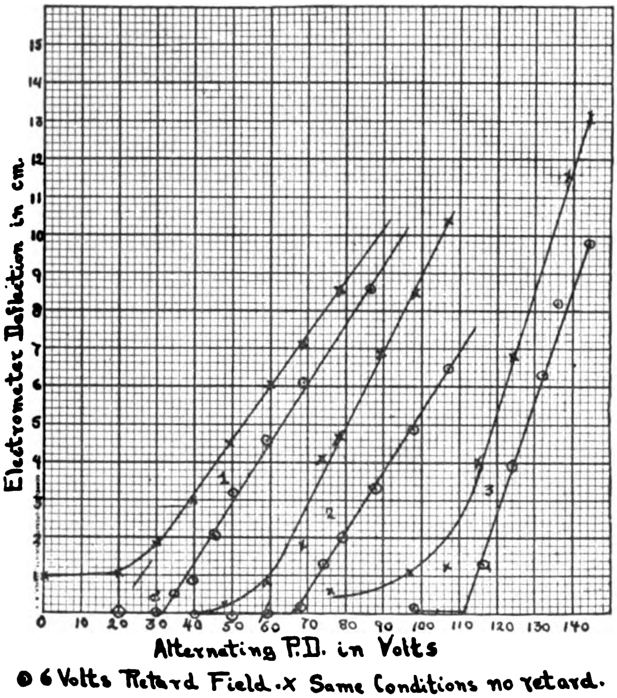

Fig. 2.

with the cells cut the axis sharply at a value close to six volts above the value obtained from the extrapolated portions of the crossed curves. This is just what was to be expected if the feet were due to ions, the effect of the retarding field being to remove the feet, and to increase the critical voltage by six volts.[1] Since the values of the mobilities obtained in the two cases are the same it is immaterial which method is used in measurement, both the cells and extrapolation giving correct values. The important point is that *these feet are not an essential attribute of electron mobility curves*, and are due to causes other than peculiarities of the electrons.

3 and 4. The improvements numbered 3 and 4 are self evident. As regards 3 it might be pointed out in passing that the inaccuracies present in the measurements of mobilities in N_2 made it impossible to detect the gradual contamination of the gas which remained in the metal chamber

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[1] The latter will obviously cease to be true when the fixed potential becomes an appreciable fraction of the critical voltage. However at the critical voltages below 20 volts the asymptotic feet are generally negligible, in pure H_2, and retarding fields may be dispensed with.

more than three or four days. This contamination caused changes in the mobility of less than ten per cent., and these occurred chiefly in the case of mobilities taken with low fields where the impurities were most active. Thus the mobilities at a given pressure in N_2 seemed to be quite reproducible over several days when high fields were used, while those at low fields showed a change. With the inaccuracies due to other causes of the same magnitude superimposed on this effect it became impossible to correlate it with the ageing of the gas. In H_2 where the precision was far higher, such a change at once became evident.

The hydrogen used came from a commercial tank and was carefully purified by passing over hot copper, NaOH, $CaCl_2$, through two tubes of P_2O_{50}, and through two traps cooled with liquid air. Spectroscopic examination showed only H_2 and Hg present, though it is doubtful how delicate this test was. The procedure of measurement was precisely that followed in the case of N_2. The mobility constant K, as computed from $K = (2.2nd^2/760 V_0)p$, was plotted as ordinate against the value of V_0 as abscissa as before. The points thus obtained under the best conditions are shown in Fig. 3. It is seen that in H_2 the mobility varies in much the same manner as it did in N_2. The full lines represent an attempt to fit an equation of the form $K = a/(b + V_0)$ to the points obtained for the pressures 635, 303, 151, and 73 mm. respectively. The dotted lines represent an equation of the form

$$K = \left(\frac{a}{b + V_0}\right)^{3/4}$$

applied to the same points. The equations fit the points nearly equally well, the dotted curve showing perhaps a slightly better fit. In the case of the full line curves, the curves for different pressures fall quite closely into a family of curves whose equation is

$$K = \frac{2.74 \times 10^6}{399 + \frac{V_0}{d}\left(\frac{760}{p}\right)^{3/4}}.$$

The attempt to incorporate the dotted curves for different pressures into a family of curves of the form

$$K = \left(\frac{1.09 \times 10^7}{81.3 + \frac{V_0}{d}\left(\frac{760}{p}\right)^{5/8}}\right)^{3/4}$$

was nearly as successful. Thus we must conclude that the equation

$$K = \frac{2.74 \times 10^6}{399 + \frac{V_0}{d}\left(\frac{760}{p}\right)^{3/4}}$$

seems to represent the observed results with the greatest accuracy. Here K is the mobility, p the pressure in mm., V_0 the critical voltage in volts, and d the plate distance in cm.

This equation for H_2 differs from that for N_2,

$$\left(K = \frac{5.71 \times 10^5}{21 + \frac{V_0}{d}\left(\frac{760}{p}\right)}\right),$$

in form only in that the pressure ratio $(760/p)$ in the case of H_2 is raised to the 3/4 power, while the power of $760/p$ in N_2 is 1. It seems likely that this difference is due to the uncertainty of the earlier measurements in N_2. For by applying the correction to the results in N_2 indicated by the conditions of the improved technique the curves obtained show changes which would make the factor $(760/p)$ in the present equation become $(760/p)^{3/4}$.

The theoretical equation for the mobility of electrons in a gas where they make partially elastic impacts with gas molecules as suggested by Townsend[1] is of the form

$$K = \frac{.815eL}{mc\sqrt{1 + \frac{.575V_0eL}{me^2d\sqrt{f}}}},$$

where L is the electron mean free path, e its charge, m its mass, c its velocity of thermal agitation, and f the fraction of its energy lost at each impact. This equation demands that the mobility K should vary as

$$K = \left(\frac{a}{b + \frac{V_0}{d}\left(\frac{760}{p}\right)}\right)^{1/2},$$

where a and b are functions of L and f. As the experimental equation has the form above one may then conclude that in H_2 as in N_2 either the mean free path (L) of the electron, its loss of energy on impact f, or perhaps both of these quantities, vary as a function of the energy of the electron, *i.e.*, depend on V_0/d and $760/p$. No conclusion can at present be drawn as to which one of these factors is the more important variable, though it is hoped that results obtained in He may shed light on this question. The results of Ramsauer,[1] Mayer,[2] and Townsend[3] on the variation of the electronic mean free path in argon with the electron velocity, and the results obtained by Townsend[3] on the variation of the mean free paths with the electron velocity in other gases, indicate that a variation of the mean free path may possibly be the cause of the deviation of the observed mobilities from those demanded by the theory.

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[1] L. B. Loeb, PHYS. REV. (N. S.), 19, 1922 (24).
L. B. Loeb, Proc. Nat. Acad. Sciences, 7, 1921 (307).

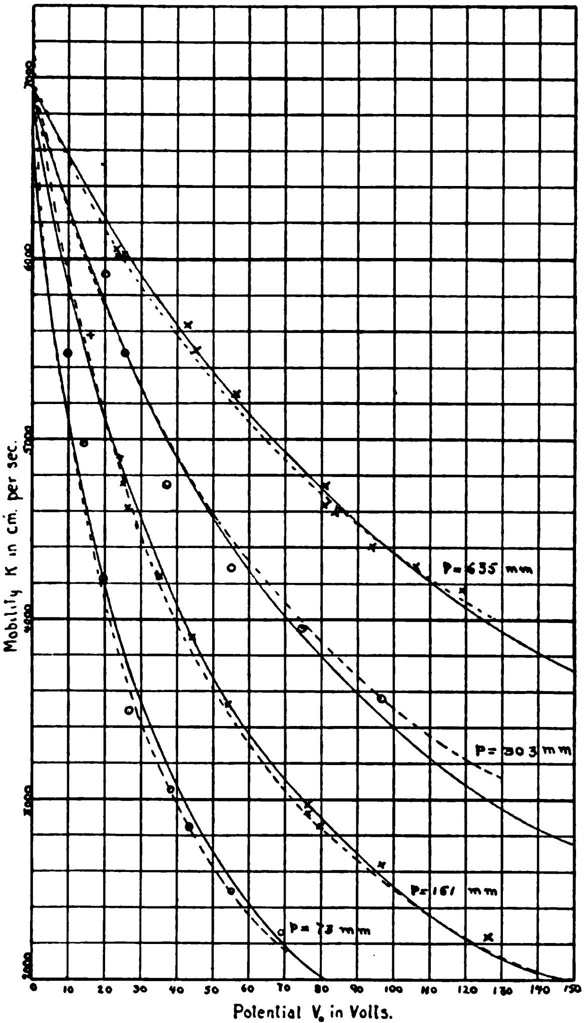

Fig. 3.

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[1] C. Ramsauer, Ann. d. Phys., 64, 1921 (513).

[2] H. F. Mayer, Ann. d. Phys., 64, 1921 (451).

[3] J. S. Townsend and V. A. Bailey, Phil. Mag., 43, 1922 (593).

In the case where the field becomes very small (*i.e.*, for V/d approaching 0), the observed equation for the variation of K with V_0 approaches a constant value $K_0 = a/b$ which may be compared with the value of K_0 predicted by the kinetic theory. For in this case the electron absorbs no appreciable energy from the field, and its energy is that of the agitation of the molecules. The kinetic theory gives K_0 for electrons as

$$K_0 = \frac{.815e}{m} \frac{L}{c}.$$

Computing K_0 for N_2 it was found that the observed value was about 3.9 times as great as the computed value. In the case of H_2, K_0 computed is 13,060, while K_0 observed turns out to be but 6860. The observed mobility is then .53 the computed one. This difference of observed and computed values must be interpreted as meaning that the mean free paths assumed by the kinetic theory differ from those actually existing. For the mean free paths are the only factors of the equation which could vary in this case.

Thus the mean free path of electrons in N_2 is about four times that assumed by kinetic theory, a result similar to that found by Townsend, Mayer, and Ramsauer, for argon at much higher electron velocities; while the mean free path of electrons in H_2 is .53 that assumed by kinetic theory. An explanation for the low value of the mean free path found in hydrogen may be sought in the explanation given to the low values of the mobilities found for *gas ions* on the "small ion" theory. On this theory the reduction of the mobility is explained by assuming that the field of the electron acts on the surrounding gas molecules, and so by either losing momentum it has gained in the field, or by making its collisions with molecules more frequent, it effectively seems to shorten its mean free path. Why H_2 should show this latter effect while in nitrogen this effect seems to be absent furnishes a problem for the future.

NATIONAL RESEARCH FELLOWSHIP,
RYERSON PHYSICAL LABORATORY,
June 12, 1922.

THE SCATTERING OF X-RAYS BY CRYSTALS.

By G. E. M. Jauncey.

Synopsis.

Scattering of X-rays by Crystals (Rocksalt and Calcite), Metal (Aluminum) and Amorphous Solid (Glass).—Both homogeneous rays (K_a of Mo obtained by preliminary reflection from a rocksalt crystal) and heterogeneous rays direct from a Mo or W target (70 to 110 kv.) were used, and *scattering curves* were obtained by measuring the ionization for various angles of scattering. On account of the small intensity of the scattered radiation, incident beams of 15′ to 3° width and a scattered beam of 6° width were required even with a sensitive Compton electrometer. For angles from 50° to 150° the curves obtained for the crystals are of the same shape as those for Al and glass, each curve showing a minimum at about 100°; but for angles below 50° the crystal curves fall below the others and each shows a maximum at a larger angle, between 15° and 30°, depending on the wave-length. In addition to the general scattering at all angles, there appear, for the crystalline substances, maxima corresponding to the Laue spots. When correction for the absorption of the crystal is made, for which a formula is given, the scattering in a particular direction is found not to depend on the orientation of the crystal. This indicates that the atoms are isotropic. As was to be expected the scattered radiation was softer than the primary. For the width of x-ray beams used the total energy scattered in all directions was an appreciable fraction (0.70 for homogeneous Mo K_a rays on calcite) of the energy reflected in a first order spectrum line. *Comparison with the Debye theory* shows fair agreement only in the case of rocksalt for angles greater than 60°. For calcite there is no agreement and the prediction that the scattering by amorphous substances should be quite different from that by crystals is not verified. Applying the Thomson formula, however, the number of electrons per molecule for each crystal has been calculated from the relative amount of energy scattered at 90° and comes out of the right order of magnitude.

In his paper on the "Interference of Roentgen Rays and Heat Motion," Debye[1] states that the regular reflection of x-rays from a crystal surface is accompanied by diffusely scattered radiation which is the most intense at those angles at which the intensity of the regularly reflected radiation is least. He finds that, if the crystal is set at such angles as to reflect a particular x-ray spectrum line in different orders, and if the ionization chamber is set to receive the reflected beam in each order, the heat motions of the atoms should cause the intensity of the different orders to fall off as the number of the order increases. On the other hand, this thermal agitation causes the intensity of the diffusely scattered radiation to increase as the angle with the primary beam of x-rays increases. In another paper,[2] Debye discusses the effect of the regular arrangement of the electrons in the atoms upon the x-ray scattering when the atoms themselves have the random arrangement characteristic of amorphous substances. Comparing these two papers, it appears that the general scattering by crystals should be quite different from that by amorphous substances. The present experimental investigation was undertaken primarily to see if the difference predicted by Debye really occurs.

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[1] P. Debye, Ann. der Phys., Band 43 (1914), pp. 49–95.

[2] P. Debye, Ann. der Phys., Band 46 (1915), pp. 809–823.

EXPERIMENTAL METHODS.

If the primary x-rays strike a crystal face at a glancing angle θ, the regularly reflected rays occur at an angle 2θ with the primary rays. In the experiments described in this paper the ionization chamber instead of being set at an angle 2θ with the primary rays is set at some other angle ϕ. The intensity of the diffuse scattering in different directions is thus measured, and curves showing the variation of the intensity of the scattered radiation with the angle are obtained. These curves are then compared with similar curves obtained using amorphous substances.

In the first experiments, x-rays from the molybdenum target of a Coolidge tube, after reflection from rocksalt to isolate the K_α line, fell upon the crystal under investigation. The second crystal was now placed at the appropriate angle θ for the regular reflection of the molybdenum K_α line in either the first or second order (see Fig. 1). Keeping the crystal in this position, readings were taken with the ionization chamber at various angles ϕ between 8° and 90°. The tube was operated by an x-ray transformer at about 70 kilovolts, and the current, 4 milliamperes, was controlled by a Victor current stabilizer. It was found that with this stabilizer it was not necessary to employ a balance method for measuring the x-rays.

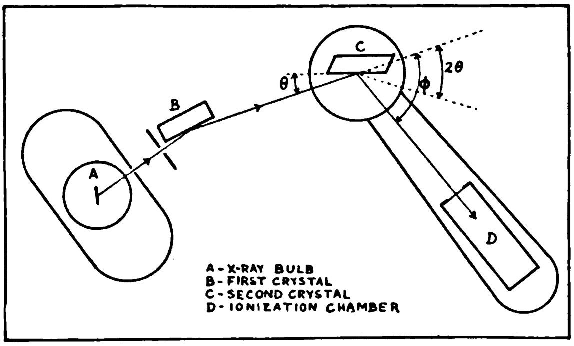

Fig. 1.

The ionization chamber was filled with a mixture of methyl iodide vapor and air, and the ionization current produced in the ionization chamber measured by the deflection of a Compton electrometer operating at a sensibility of about 2500 millimeters per volt. With this two-crystal method the deflection due to the diffuse scattering of the x-rays from the second crystal was only a few millimeters per minute. As there was some difficulty in this method of eliminating small deflections due to stray scattering, a set of readings was taken with the second crystal in position and another set at the same angles with the second crystal removed. The reading with the second crystal removed was subtracted from the reading with the second crystal in position for each angle and the difference plotted against the angle of the ionization chamber. In this way the effect of stray scattering was eliminated.

In many of the experiments, especially those in which the scattering at large angles was measured, the first crystal of Fig. 1 was removed, and the x-rays fell directly upon the crystal under investigation. Though this single-crystal method employs heterogeneous x-rays, it was necessary in certain cases where the double-crystal method would have given an intensity too small for accurate measurement. With the single-crystal method, x-ray tubes with molybdenum and tungsten targets were used. In the case of the molybdenum tube the crystal, either rocksalt or calcite, was placed at an angle to reflect the molybdenum K_a line in the first order. With the tungsten tube the crystal was set to reflect only the general radiation, but was operated at different potentials, 70, 95 and 110 kilovolts.

The aluminum window of the ionization chamber which received the scattered x-rays from the crystal under investigation was 3 cm. high and 1.5 cm. wide. The distance of this window from the axis of the spectrometer was 14.3 cm., so that the angle subtended by the window at the face of the scattering crystal was 6°. Using the two-crystal method, when both crystals were set to reflect the molybdenum K_a line and the ionization chamber was placed so as to receive the regularly reflected beam from the second crystal, it was found that by rotating the second crystal through about 30′ on either side of the maximum the intensity of the reflected line fell to half value, so that the angular width of the beam incident on the second crystal can be taken at approximately 1°. With the single crystal method, beams of angular widths 3°, 45′ and 15′ were used.

Experimental Results.

Double-Crystal Method.—The scattering curves obtained with rocksalt as the second crystal when set to reflect the molybdenum K_a line in the first and second orders are shown as Curves *a* and *b* respectively of Fig. 2. Curve *c* is a similar curve for calcite when set to reflect the line in the first order. Supplementary experiments showed that the beam incident upon the second crystal contained no appreciable x-rays of wave-length differing considerably from the K_α line. It will be noted that, even with the wide slits which were used, the intensity of the diffusely scattered radiation is only a fraction of 1 per cent. as great as the intensity of the first order reflection. In the case of calcite there is distinct evidence of a line reflected into the ionization chamber at 79°, though the crystal face is at a glancing angle of 6° 45′ with the incident beam.

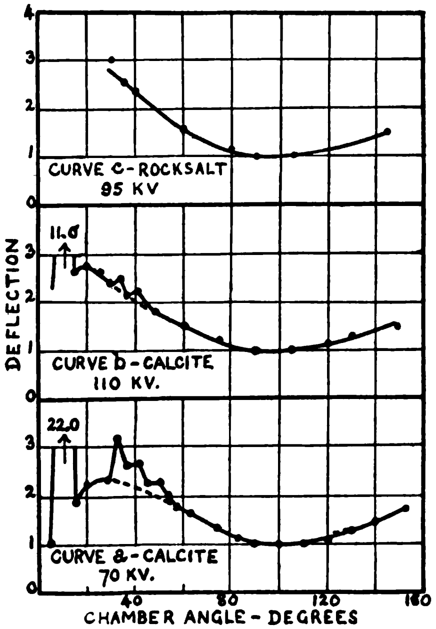

Fig. 2.

It seemed possible that the intensity of the x-rays scattered by a crystal in a certain direction ϕ might be altered if the second crystal were turned out of the position in which it regularly reflected the molybdenum K_α line. It is known that the absorption coefficient of homogeneous x-rays in a crystal is increased when the rays are incident at the proper angle. Due to this increase of absorption coefficient the x-rays incident on the crystal will not penetrate so far into the crystal, and there should be less scattering. The chamber was accordingly set at an angle of 65° while the rocksalt crystal was set at various angles between 6° 20′ and 11° 20′. Fig. 3 shows the curve obtained. It will be seen that there is no evidence of a minimum at 7° 20′, the angle at which the K_α line is reflected. The explanation of this is probably that the beam incident on the second crystal has a considerable angular width. It is only those rays which strike the crystal at the correct angle whose absorption coefficient is increased. With a wide beam such as used in these experiments only a small fraction of the incident beam suffers this extra absorption.

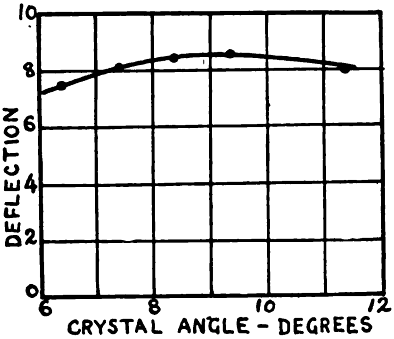

Fig. 3.

The ratio of the intensity of the x-rays scattered at 90° to the energy of the beam of x-rays incident upon the second crystal is of considerable theoretical importance. The ratio is so small that it was necessary to obtain first the ratio of the intensity of the diffusely scattered x-rays to the energy of the regularly reflected rays when the crystal was set to reflect the molybdenum K_α line in the first order. The current through the x-ray tube was then greatly reduced, and the ratio of the deflection due to the regular reflection to that when the incident rays entered directly into the ionization chamber was obtained. The product of these ratios gives the ratio of the intensity of the x-rays scattered at 90° to the energy of the primary rays. The results are shown in the fourth column of Table I. Because of the small deflections given by the scattered x-rays these ratios are only approximate.

Single-Crystal Method.—When the direct radiation from the molybdenum tube fell upon a crystal of rocksalt, Curve *a*, Fig. 4, is obtained. In addition to the general scattering there appears a regularly reflected beam at 51°, though the crystal face makes an angle of 7° 20′ with the primary beam, the angular width of which was 45′. The corresponding curve for calcite is shown in Curve *b*, Fig. 4. In this case the angular width of the primary beam was 3°. With the calcite crystal there are regularly reflected beams at 28°, 38° and 79°. The line at 79° was previously noticed in Curve *c*, Fig. 2. These curves for rocksalt and calcite are drawn to have equal ordinates at 90° and are typical of all the curves obtained. There is scattering at all angles, but superimposed

TABLE I.

Intensity of X-Rays Scattered at 90°.

Crystal.	Nature of X-Rays.	Linear Absorption Coefficient in Crystal.	$\frac{\text{Intensity of Scattered Rays.}}{\text{Energy of Primary Rays.}}$.	Apparent Number of Electrons per Molecule.
Rocksalt......	Homogeneous Mo-K_α Line	17.5	1.4×10^{-5}	16.3
Calcite........	Homogeneous Mo-K_α Line	25.0	2.0×10^{-5}	47.6
Rocksalt......	Heterogeneous Tungsten Tube	1.39	4.0×10^{-4}	29.7
Calcite........	Heterogeneous Tungsten Tube	0.88	5.3×10^{-4}	34.2
Aluminum Sheet.......	Heterogeneous Molybdenum Tube	6.7	5.2×10^{-5}	8.5

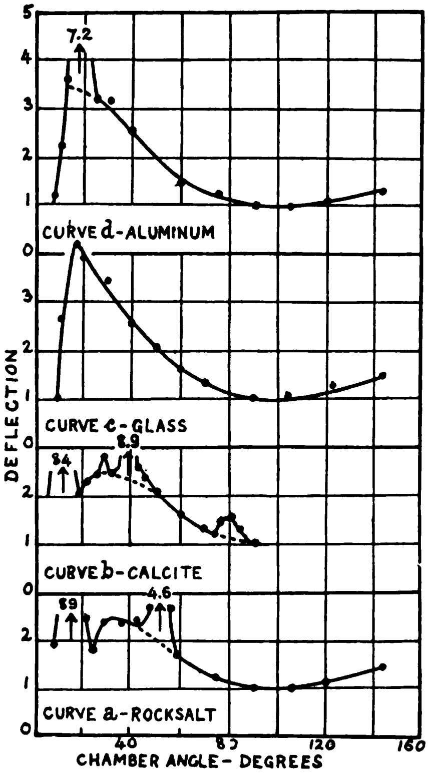

Fig. 4.

on the general scattering there is regular reflection at particular angles when the crystal is set at a certain angle.

An absorption experiment showed that the rays causing the large deflection at 38° with calcite are the molybdenum K_a rays. The humps at both 38° and 79° disappear if the orientation of the crystal is slightly changed, showing that these are undoubtedly regular reflections. There is however no such evidence of regular reflection at angles where no humps appear on the curve.

The Curves *c* and *d* of Fig. 4 were obtained when plates of glass and aluminum respectively were used in place of the crystal, the glancing angle for glass and aluminum being 8°. Otherwise these curves were obtained under the same conditions as the curves for the crystals. In addition to the general scattering, the curve for the aluminum shows evidence of regular reflection at 19°. This is due to the fact that aluminum is not amorphous but an agglomeration of minute crystals, and a powdered crystal effect is obtained.

A variation in the experiment with calcite was made by setting the chamber at an angle of 56° and turning the crystal from 5° to 56°. The curve so obtained is shown in Curve *b*, Fig. 5. Regularly reflected beams are obtained when the crystal is at 13° and 28°. The slope of the portion *AB* of the curve is due to the fact that at small angles of the crystal part of the primary x-rays pass by the crystal without striking it.

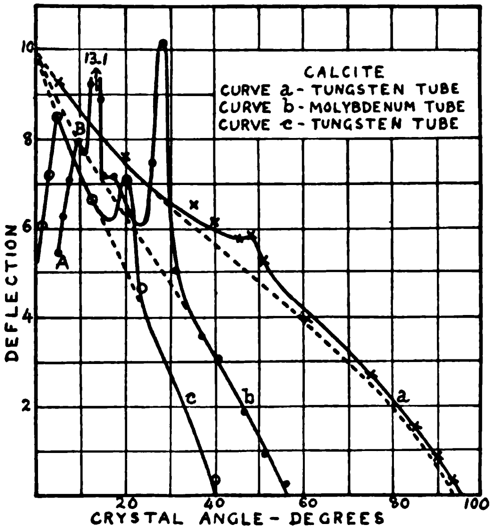

Fig. 5.

Using a tungsten tube, Curves *a*, *b* and *c* of Fig. 6 were obtained, the crystal angle in each case being 5°. These curves are reduced to the same ordinate at 90°. Curve *a* is for calcite with the tube operated at a potential of 70 kilovolts, while the potential for Curve *b* was 110 kilovolts.

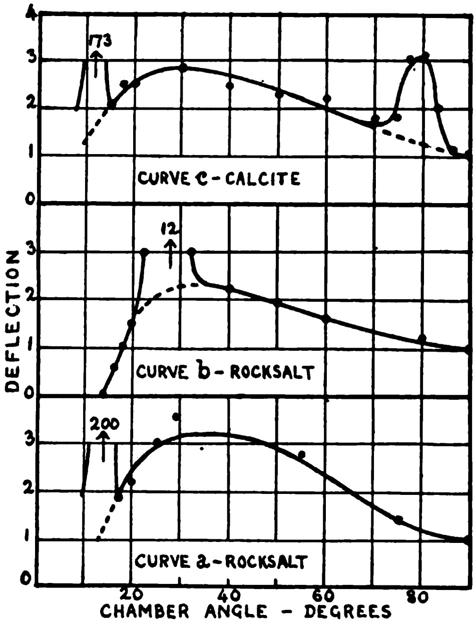

Fig. 6.

Regular reflection appears at 34° and 40° in each case, but with the greater potential the intensity of the general scattering is relatively much stronger. The angular width of the primary beam was 15′. Curves *a* and *c* of Fig. 5 were obtained by setting the chamber at 94° and 40° respectively and turning the crystal.

The quality of the radiation diffusely scattered by calcite was tested by placing an aluminum absorbing screen alternatively in the path of the primary and of the scattered beam. It was found that the scattered rays were somewhat more readily absorbed than the primary rays which produced them. This result is in accord with the scattering measurements made by others on non-crystalline substances.[1]

The ratio of the intensity of the x-rays scattered at 90° to the energy of the primary rays was measured by a method similar to that for the homogeneous x-rays. The results are shown in the fourth column of Table I. The calcite and rocksalt crystals were set at 5° while the aluminum plate was set at 8°.

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[1] Cf. Sadler and Mesham, Phil. Mag., Vol. 24 (1912), pp. 138–149; A. H. Compton, Nature, Vol. 108 (1921), p. 366; et al.

Discussion of Results and Calculations.

The scattering curves show that crystals scatter x-rays in a manner similar to amorphous substances, but that in addition to this general scattering there are regularly reflected beams in certain directions with the crystal set at a given angle. Not all of these humps are due to spectrum lines, although some of them are. For instance the hump at 38° in Curve *b*, Fig. 4 was shown to be due to the molybdenum K_α line. In other cases, however, reflection is obtained from some plane in the crystal which will reflect a certain wave-length λ of the general radiation falling upon the crystal according to the equation $n\lambda = 2d \sin \theta$.

It might be supposed that the intensity scattered by a crystal molecule in a certain direction ϕ with the primary x-rays might depend upon the orientation of the molecule with respect to the primary rays. In other words, if the ionization chamber is set at an angle ϕ and the crystal turned there might be a difference in the molecular scattering in the direction ϕ as the crystal is turned. Curves for this case have been obtained in Fig. 5. Those curves are of course for the scattered radiation which gets out of the crystal. Let us suppose that the linear scattering coefficient of the crystal for a direction ϕ is s_ϕ irrespective of the orientation of the crystal relative to the primary beam. It can be shown that, if the linear absorption coefficient of the primary x-rays in the crystal is k (the slight difference between k for the primary and for the scattered rays being neglected), the intensity of the scattered x-rays leaving a thick crystal in a direction ϕ is

$$(1) \qquad \frac{s_\phi I_0}{k} \cdot \frac{\sin(\phi - \theta)}{\sin(\phi - \theta) + \sin\theta},$$

where I_0 is the energy of the primary x-rays and θ is the glancing angle of the primary rays upon the crystal face. If ϕ is kept constant, formula (1) may be written in the form

$$(2) \qquad \text{constant} \times \frac{\sin(\phi - \theta)}{\sin(\phi - \theta) + \sin\theta}.$$

The broken curves in Fig. 5 are obtained by plotting values of (2) against θ for $\phi = 90°$, 56° and 40° respectively, the appropriate value of the constant being taken in each case. It is seen that the experimental curves correspond with the theoretical curves excepting for the humps due to regular reflection. The result implies that the intensity of the rays scattered by a crystal molecule in a given direction ϕ does not depend upon the orientation of the crystal, and that therefore the atoms of the crystal are nearly isotropic.

The scattering curves should be corrected for absorption in the crystal in order to give the true molecular scattering in various directions. If each of the ordinates of each of the experimental scattering curves is divided by formula (2), the true scattering curves shown in Fig. 7 are obtained, the humps due to regular reflection being omitted. These curves are drawn so as to have the same ordinate at 90°. Curves a, b, c and d are for heterogeneous x-rays from a molybdenum tube, while Curves e, f and g are for heterogeneous x-rays from a tungsten tube. It is seen that the curves are practically identical for the range $\phi = 50°$ to $\phi = 150°$. In this range the crystal curves (a, b, e, f and g) coincide with the curves for aluminum and glass (c and d). Below 50° the crystal curves all fall below the aluminum and glass curves. The crystal curves all reach a maximum between 15° and 30°. The curves for calcite and rocksalt, when the primary rays are homogeneous molybdenum K_α rays, are not shown but have the same general characteristics as the curves shown. Curves e and f are for the same calcite crystal and for the same tungsten tube, the only difference being that the potential for Curve e is 70 kilovolts while that for Curve f is 110 kilovolts. It appears as though the maximum is shifted to the smaller angles for the shorter wave-lengths.

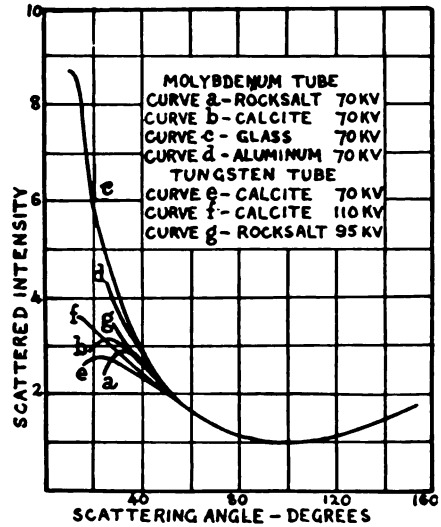

Fig. 7.

It would be interesting to examine the shape of the scattering curves for small angles. It is known that the scattering curves for amorphous substances slope down towards zero for small angles, but the maximum occurs at much smaller angles than do the maxima for crystals in the present experiments. For instance Curve *c* which is for glass does not show a maximum above 11° whereas calcite Curve *b* shows a maximum at 25° even though both curves are for a molybdenum tube operated at a potential of 70 kilovolts. The experimental difficulties when working at small angles necessitate the abandonment of this inquiry at this time.

According to Debye[1] the intensity of the x-rays scattered in a direction ϕ from a crystal should be equal to that from an amorphous substance multiplied by $(1 - e^{-M})$, where

$$M = \frac{0.569 \times 10^{-12}}{A\Theta\lambda^2} \times (1 - \cos\phi) \times \frac{F(z)}{z}$$

when there is no zero-point energy and

$$M = \frac{0.569 \times 10^{-12}}{A\Theta\lambda^2} \times (1 - \cos\phi) \times \left[\frac{F(z)}{z} + \frac{1}{4}\right]$$

when there is a zero-point energy. In these z is the ratio of the characteristic temperature Θ of the crystal to its experimental temperature, A its atomic weight, λ the wave-length of the incident homogeneous x-rays, and $F(z)$ is a function of z which Debye evaluates. The value of the factor $(1 - e^{-M})$ has been found for both clacite and rocksalt when the incident wave-length is 0.717 Å. U., which is the wave-length of the molybdenum K_α line,[2] and the room temperature is 290° K. A. H. Compton[3] gives the characteristic temperatures of calcite and rocksalt as 910° K. and 260° K. respectively. The atomic weight of calcite is taken as the average atomic weight, viz., 20. The value of $(1 - e^{-M})$ for a certain value of ϕ is divided by the value for $\phi = 90°$. The curve obtained is shown as Curve *a*, Fig. 8. There are two possible

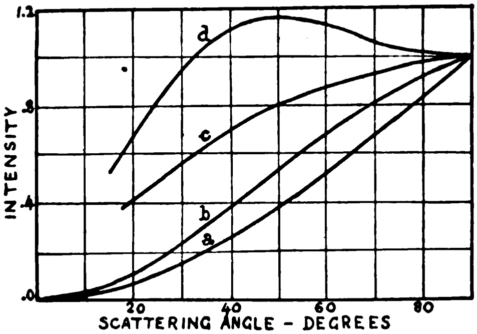

Fig. 8.

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[1] Loc. cit.

[2] Kaye and Laby, Physical and Chemical Constants, 4th Ed., p. 99.

[3] A. H. Compton, Phys. Rev., Second Series, Vol. 9 (1917), p. 47.

curves, one for the case where there is no zero-point energy and the other for the case where there is a zero-point energy. The two curves, however, are very close together and the mean curve is the one shown. If each ordinate of Curve *c*, Fig. 7, which is for glass, is multiplied by the corresponding ordinate of Curve *a*, Fig. 8, the theoretical scattering curve for a crystal of calcite is obtained. This is shown as Curve *c*, Fig. 8. Curves *b* and *d*, Fig. 8, are the curves for rocksalt, the average atomic weight of rocksalt being taken as 29. It will be seen that Curve *d* which is the theoretical scattering curve for rocksalt coincides fairly well with the experimental curve for the range 90° to 60°, but below 60° there is a great discrepancy between the theoretical and experimental curves. In the case of calcite the curves do not coincide at any place.

According to J. J. Thomson[1] the intensity of x-rays falling on 1 cm.[2] at a distance R from the scattering substance is

$$\frac{Ne^4}{R^2m^2c^4}\cdot\frac{1+\cos^2\phi}{2}\cdot pI_0, \tag{4}$$

where p is the number of electrons per atom (or molecule), N is the number of atoms (or molecules) per unit volume and I_0 is the energy of the primary rays. This is also the formula obtained by Debye[2] for the case of an amorphous scattering substance when the wave-length of the x-rays is small compared with the radius of the atomic electron ring. If it is assumed that the absorption coefficient of the scattered x-rays is equal to that of the primary x-rays, then the total intensity of the rays entering the ionization chamber from a thick crystal when the crystal angle is θ and the chamber angle is 90° can be shown to be

$$I_{90}=\frac{SNe^4}{R^2m^2c^4}\frac{p}{2k(1+\tan\theta)}I_0, \tag{5}$$

where S is the area of the window of the ionization chamber and k is the linear absorption coefficient of the x-rays in the crystal. Knowing the experimental value of I_{90}/I_0 and the value of k, p the number of electrons in the atom (or molecule) of the scattering crystal can be found. The linear absorption coefficients of molybdenum K_α rays in rocksalt and calcite were not found directly but were calculated from the known coefficient for aluminum using the law that the atomic absorption of an element varies as the fourth power of the atomic number of the element. The absorption coefficients for heterogeneous x-rays were measured directly. There is considerable doubt of the coefficients for heterogeneous rays as they depend upon the thickness of crystal used. It is seen that the numbers of electrons per molecule are of the right order of magnitude, the true values for rocksalt and calcite being 28 and 50 respectively. According to Debye's theory of crystal scattering the factor $(1 - e^{-M})$ should enter into the intensity scattered. The absolute value of the factor for scattering at 90° from calcite for a wave-length of 0.717 Å. U. (molybdenum K_α line) is 0.092 for no zero-point energy and 0.227 for zero-point energy, that is, the intensity scattered at 90° by a crystal of calcite should be either about one tenth or one fifth of that scattered by an amorphous substance of equal molecular weight. The fact that p comes out of the right order of magnitude and not one tenth or one fifth of the correct value shows that Debye's theory falls far short of explaining the experimental facts for calcite. For rocksalt the value of $(1 - e^{-M})$ for scattering at 90° and for a wave-length 0.717 Å. U. is 0.73 for no zero-point energy and 0.82 for zero-point energy, the two experimental values for rocksalt being 0.56 and 1.06. Hence in the case of rocksalt the theory as far as the scattering at 90° is concerned is not opposed to the facts.

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[1] J. J. Thomson, Conduction of Electricity through Gases, 2d Ed., p. 325.

[2] Loc. cit.

The discrepancy between Debye's theory of scattering and the observed results in the case of rocksalt is remarkable because in another direction Debye's theory has received confirmation. According to Debye the energy of a regularly reflected line should be proportional amongst other things to e^{-M}. This was tested by W. H. Bragg[1] in an experiment where he heated a crystal of rocksalt and observed the energy of the rhodium line as reflected by the crystal (1) when the crystal was at a temperature of 288° K., and (2) when the crystal was at 643° K. The observed ratio of the energies was equal to the ratio as calculated from the theory. This might not have been so remarkable if the glancing angle in Bragg's experiment had been above 30°, making the chamber angle above 60°, as it is between 60° and 90° in my experiments that the scattering curve of rocksalt as found experimentally agrees to some extent with that indicated by the theory. However Bragg's experiments were done at glancing angles between 12° and 13° 30′ in the case of second order reflection and between 18° 30′ and 20° in the case of the third order reflection. In the former case the chamber angle is between 24° and 27° while in the latter case the chamber angle is between 37° and 40°. This is just the range where there is very great discrepancy between Debye's theory as applied to scattering from crystals and the experimental results of this present paper. For this reason it is a matter of great interest to test the temperature effect on the intensity of x-rays scattered by a crystal. This investigation however will be left for another paper.

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[1] W. H. Bragg. Phil. Mag., Vol. 27 (1914), pp. 881–899.

From the true scattering curves of Fig. 7 it is possible to calculate the ratio between the energy of the regularly reflected beam at $\phi = 2\theta$ to the total energy .scattered. The energy scattered between the two cones of semi-angles $\phi - (\delta\phi/2)$ and $\phi + (\delta\phi/2)$ is given by

$$\frac{2\pi R^2 \sin \phi \, \delta\phi}{S} \cdot y, \tag{3}$$

where y is the ordinate of one of the curves in Fig. 7 for a particular value of ϕ, R is the distance of the window of the ionization chamber from the crystal, and S is the area of the window, and $\delta\phi$ is 6°. Values of (3) are calculated for each interval of 6° and these added for the range $\phi = \phi_1$, and $\phi = \phi_2$, thus giving the total intensity of true scattering between the two cones whose semi-angles are ϕ_1 and ϕ_2. The results for calcite are shown in Table II. The ratio is calculated for homogeneous x-rays on the assumptions that the absorption coefficient in the crystal is the same when the crystal is in a reflecting position as when it is thrown out of this position, and also that the absorption coefficient of the scattered x-rays is equal to that of the primary x-rays. The ratio is therefore only an approximation.. When the ratio is calculated for heterogeneous radiation consisting of the molybdenum K_α line plus general radiation a difficulty arises in that the absorption coefficient of the regularly reflected line is quite different from that of the scattered radiation. In the case of the x-rays coming from a tube with a molybdenum target the mass absorption coefficient of the general scattered radiation was 1.51 while that of the molybdenum K_α line was 5.17. A different value of k in formula (1) must be used for the line from that for the general scattered radiation.

TABLE II.

Proportion of X-Rays Regularly Reflected.

Nature of X-Rays.	ϕ_1.	ϕ_2.	$\frac{\text{Energy of Regularly Reflected X-Rays.}}{\text{Energy of Scattered Radiation}}$
Homogeneous Mo K_α line.....	14°	93°	2.85
Heterogeneous Mo K_α line plus General Radiation..........	15°	153°	0.66

Calcite Crystal Set for First Order Reflection of Mo K_α Line.

There is also scattering of the homogeneous x-rays in the ranges 0° to 14° and 93° to 180°. The scattering throughout the whole range 0° to 180° is about double of that in the range 14° to 93°. The energy of the regularly reflected line is therefore about 1.43 times that of the total scattering. This is for the case where the angular width of the primary beam is about 1°. For heterogeneous x-rays the proportion reflected is much less, being 0.66 of the amount scattered in the range 15° to 153°. Taking the whole range 0° to 180°, the energy reflected in the line is about one half of the total energy scattered. This is for an angular width of the primary beam equal to 45′. For higher orders of reflection these ratios are much smaller and are smaller still for the case where the crystal is not set to reflect a line but general radiation. The total energy scattered from a crystal is less than that scattered from glass. Comparing calcite and glass using a molybdenum tube and interpolating Curves *b* and *c* of Fig. 7 for the angles 0° to 15°, the ratio of the total energy scattered by the crystal to that scattered by the glass for the range 0° to 150° is 0.85. It was thought that the regular reflection from a crystal might take place at the expense of the general scattering and that the difference between the energy scattered by glass and by a crystal might be equal to the energy of the regularly reflected radiation. This however is not the case.

Summary.

The scattering of x-rays by the crystals calcite and rocksalt has been examined and the following results found:

1. The scattering curves for rocksalt and calcite are of the same shape as the curves for the amorphous substances glass and aluminum for the range 50° to 150° with the direction of the primary rays. The minimum of all the curves occurs at about 100°.

2. For scattering angles below 50° the crystal curves fall below those for the amorphous substances. The crystal curves reach a maximum between 15° and 30°, the position of the maximum being at smaller angles for smaller wave-lengths. The maximum in the case of amorphous substances occurs at much smaller angles than in the case of the crystals.

3. From the ratio of the intensity of the x-rays scattered at 90° to the energy of the primary rays the number of electrons per molecule of each crystal has been calculated by means of Thomson's formula. The numbers as calculated are of the right order of magnitude.

4. The x-rays scattered from crystals are softer than the primary x-rays, in this way resembling the x-rays scattered from amorphous substances.

5. A comparison between the experimental results and the theory of crystal scattering as developed by Debye has been made. It is shown that Debye's theory falls far short of explaining the observed facts. In the case of rocksalt there is fair agreement between the intensity scattered at 90° and that predicted by Debye, but at angles below 60° the difference between theory and experiment becomes great. For

calcite there is no agreement whatever between theory and experiment. This may be due to the fact that $CaCO_3$ is a more complicated molecule than NaCl.

6. In addition to the general scattering at all angles from a crystal, there appear Laue spots at particular angles.

7. The energy of x-rays scattered by a crystal in all directions is an appreciable fraction of the energy of a regularly reflected line.

8. The intensity of x-rays scattered in a certain direction is independent of the orientation of the crystal which suggests that the atoms are nearly isotropic.

9. The total scattering was not appreciably changed by turning the crystal from a position where a spectrum line was regularly reflected to a position where the line was not reflected.

In conclusion the author wishes to express his thanks to Professor A. H. Compton for his interest and aid in the preparation of this paper.

Washington University,
St. Louis, Mo.,
June 8, 1922.

THE EFFECT OF TEMPERATURE ON THE SCATTERING OF X-RAYS BY CRYSTALS.

By G. E. M. Jauncey.

Synopsis.

Variation of the Scattering of X-Rays by Rocksalt and Calcite with Temperature.—Using x-rays from the *W* target of a Coolidge tube operated at 95 kv., the ratio of the radiation scattered from a crystal at 295° C. to that scattered at the same angle from the crystal at 17° C. was found to be: 1.33 and 1.18 ± .10 for rocksalt and angles of 15° and 30° respectively, and 0.99 and 1.03 ± .04 for calcite and angles of 30° and 73° respectively. Thus there is a marked effect for rocksalt but apparently none for calcite, which seems to scatter x-rays like an amorphous substance. *Comparison with the Debye theory* shows that even for rocksalt the effect is considerably smaller than that theoretically predicted, whether zero-point energy is assumed or not, while for calcite the disagreement is marked.

Debye[1] has developed a theory of the scattering of x-rays in which he predicts that the intensity of the x-rays scattered in a direction ϕ with the primary rays should be proportional to $(1 - e^{-M})$, where

$$M = \frac{0.569 \times 10^{-12}}{A\Theta\lambda^2} \times (1 - \cos\phi) \times \frac{F(z)}{z}$$

for no zero-point energy, and

$$M = \frac{0.569 \times 10^{-12}}{A\Theta\lambda^2} \times (1 - \cos\phi) \times \left[\frac{F(z)}{z} + \frac{1}{4}\right]$$

for zero-point energy. In these expressions, λ is the wave-length of the x-rays, A the atomic weight, Θ the characteristic temperature of the crystal, z the ratio of the characteristic temperature of the crystal to its experimental temperature, and $F(z)$ is a function which Debye evaluates. As shown by the author in a previous paper,[2] Debye's theory falls far short of explaining the scattering curves for the crystals calcite and rocksalt obtained experimentally and it is therefore of interest to determine how the temperature affects the intensity of the x-rays scattered in a certain direction ϕ.

The crystal to be investigated was placed with its (100) face on the axis of a Bragg spectrometer as in the single crystal method described in the previous paper. In the present experiment, however, the crystal was surrounded by a heating box, supplied with mica windows. The x-rays from a Coolidge tube with a tungsten target, which was operated at a potential of 95 kilovolts in most cases and at a potential of 70 kilovolts in one case, passed through the mica windows. The crystal face was set at an angle θ, and the ionization chamber at an angle ϕ, with the primary rays, care being taken that only diffusely scattered rays and no regularly reflected rays entered the chamber. A set of 10 readings was taken at the room temperature, which was 290° K., a second set was taken at a temperature of 568° K., and a third set when the crystal had cooled to room temperature again. The average of the second set was divided by the average of the first and third sets. The results are shown in the third column of Table I. The temperature was measured with a mercury-in-glass thermometer. In order to be sure that the crystal was at the temperature of the thermometer, the readings at the high temperature were not taken until one hour after the thermometer first registered 568° K. The change of the sensitivity of the electrometer during this time was measured and allowed for.

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[1] P. Debye, Ann. der Phys., Band 43 (1914), pp. 47–95.

[2] G. E. M. Jauncey elsewhere in this issue of the Phys. Rev.

TABLE I.

$$\frac{\text{Scattered Intensity at } 568^\circ \text{ K.}}{\text{Scattered Intensity at } 290^\circ \text{ K.}}$$

Crystal	Scattering Angle.	Experimental Value.	Theoretical Value.	
			No Zero-Point Energy.	Zero-Point Energy.
Rocksalt[1].........	15°	1.33	1.87	1.65
Rocksalt[1].........	30°	1.18	1.37	1.26
Calcite[1]...........	30°	0.99	2.64	1.56
Calcite[1]...........	73°	1.03	2.03	1.25
Calcite[2]...........	73°	1.03	2.23	1.29

The theoretical values are calculated from Debye's formula. These are shown in the fourth and fifth columns of Table I. The mass absorption coefficient of the x-rays in aluminum was measured, the mean of the coefficients when the aluminum was placed in the primary and when it was placed in the scattered beam being taken. From the relation between the absorption coefficient and the wave-length given by Hewlett,[3] the effective wave-length of the scattered x-rays was found. The average atomic weight of $CaCO_3$ was taken as 20 and that of NaCl as 29. The characteristic temperatures of calcite and rocksalt[4] are 910° K. and 260° K.

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[1] Wave-length 0.28 Å. U

[2] Wave-length 0.36 Å. U.

[3] C. W. Hewlett, PHYS. REV., Second Series, Vol. 17 (1921), pp. 284–301.

[4] A. H. Compton, PHYS. REV., Second Series, Vol. 9 (1917), p. 47.

It will be seen that rocksalt shows a temperature effect, but not so large as that predicted by Debye on the assumption of either no zero-point energy or zero-point energy. Calcite on the other hand shows practically no temperature effect. The ratios in the third column are correct to 8 per cent. in the case of rocksalt and to 4 per cent. in the case of calcite. It might be argued that one is not justified in taking 20 as the average atomic weight of calcite as the atomic weights vary from 12 to 40. The ratio for zero-point energy for a wave-length of 0.28 Å. U. and scattering angle 73° has been calculated to be 1.12 for an atomic weight of 12 and 1.45 for an atomic weight of 40. The experimental value is still much less than the smaller of these two values.

These results are in accord with the results of the previous paper. There is a very rough agreement between Debye's theory, assuming a zero-point energy, and the experimental results for rocksalt, but there is no agreement for calcite. Calcite seems to act very similarly to an amorphous substance as far as scattering is concerned. This seems to indicate that the electrons in the calcite molecule which cause the scattering act more or less independently of one another.

In a recent theoretical paper by Brillouin,[1] doubt is thrown upon the validity of the theory of Debye. Brillouin intimates that the scattering from crystals may be unaffected by the temperature.

Washington University,
St. Louis, Mo.,
June 8, 1922.

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[1] L. Brillouin, Ann. de Phys., Tome 17 (1922), pp. 88–122.

THE CRYSTAL STRUCTURE OF SILVER-PALLADIUM AND SILVER-GOLD ALLOYS.

BY L. W. MCKEEHAN.

SYNOPSIS.

Crystal Structure of Silver, Gold and Palladium and of Ag-Au and Ag-Pd Alloys. —Thin ribbons of the pure metals and of seven binary alloys of each series were prepared by fusing into small ingots and then swaging, drawing and rolling to thicknesses of from 1/400 to 1/200 cm. The x-ray diffraction patterns were photographed by allowing the K-radiation of Mo to fall for 8 to 20 hours on each ribbon. It was found that all these metals and alloys have their atoms arranged in face-centered cubic lattices. The parameter a of each lattice, the edge of the cube, has the values 4.08×10^{-8}, 4.075×10^{-8} and 3.90×10^{-8} cm. for pure Ag, Au and Pd respectively. For the Ag-Pd series, the parameter is nearly a linear function of the atomic per cent. of either component and this is also true for the Ag-Au series except that for the alloys with 30, 40 and 60 per cent. Ag the values of a came out one per cent. too high. These results are for the most homogeneous and isotropic condition and are believed to be correct to within about 1/3 per cent. *The effect of annealing* at from 830 to 940° C. for an hour or more in vacuo was to increase the size of individual crystals, to render them more homogeneous and to make their orientations more isotropic. *The effect of moderate cold working*, rolling, pressing or hammering is to reduce the size of the individual crystals and to make them less isotropic.

Densities of crystals of silver, gold and palladium, computed from the above results of X-ray crystal analysis and the atomic weights, come out 10.49, 19.24 and 11.87 respectively. The Ag and Au were pure and the Pd contained only 0.5 per cent. impurity.

INTRODUCTION.

A STUDY of the arrangement of atoms in alloys which are solid solutions of the components may throw some light on the cause of the abnormally high resistivity of such alloys. This report covers somewhat completely the crystal structure in two series of alloys, those of silver with gold and palladium, which are particularly interesting in this connection because silver and gold both possess high conductivity, whereas the conductivity of palladium is much lower than that of silver. The conductivity of the alloys is not, however, treated in this report.

PREPARATION OF ALLOYS.

The component metals were all purchased from Baker and Company, and were of high purity, the silver and gold containing less than 0.01 per cent. of impurities, the palladium containing about 2 per cent. of impurities, chiefly copper and noble metals. The chemical and metallurgical processes outlined below were conducted by Mr. J. E. Harris and Mr. H. T. Reeve, both of this laboratory, who have had extensive experience in the preparation of alloys of known composition and exceptional homogeneity. All three metals were repurified chemically and obtained in finely divided form, the principal effect of these processes upon their purity being that the palladium finally contained less than 0.5 per cent. of impurities, copper, in particular, being completely removed. The metal powders were weighed, mixed, and pressed into small cylindrical rods of the desired compositions. The Ag-Au alloys were fused in an electrically heated furnace open to the air; the Ag-Pd alloys were fused on alundum or magnesia by the oxyhydrogen flame. The ingots, which weighed about 10 grams each, were swaged and drawn into wires about one millimeter in diameter. Short pieces of these wires were rolled to a thickness of from 0.0025 to 0.0050 cm., the rolling being carried farthest for alloys containing large proportions of gold, and hence having the highest absorption coefficients for x-rays. The condition resulting from these operations is indicated below by the letter *R*.

The annealing process consisted in maintaining the temperature of the sample at from 830° C. to 940° C. for an hour or more, in vacuo, in a quartz tube furnace, electrically heated. When several alloys were annealed at one time the samples were placed in individual quartz tubes, open at one end, to prevent mutual contamination. Temperatures were read by a calibrated platinum-platinum-rhodium thermocouple. The Ag-Au alloys required much longer annealing at these temperatures than did the Ag-Pd alloys, before the results indicated even fair homogeneity and isotropy. The longest time of annealing actually used was about 13 hours. The annealed condition is indicated by the letters *RA*.

In order to determine whether certain high values of a for condition *R* were due to distortion of the space-lattice by cold-working or to some other cause, the Ag-Pd alloys in condition *A*, were rerolled after the x-ray examination so as to reduce the thickness by from 30 to 50 per cent. The increase in stiffness caused by this second rolling was very noticeable. The condition is indicated by the letters *RAR*. Finally, after examination in condition *RAR*, these same strips were reannealed and again examined. This final condition is indicated by the letters *RARA*.

METHOD OF X-RAY ANALYSIS.

The apparatus used has been fully described by Davey,[1] and only a brief statement to define the experimental conditions will here be given. The K-radiation of molybdenum, sufficiently isolated for photographic purposes by ZrO_2 filters, is allowed to fall, for from 8 to 20 hours on the face of a thin ribbon of the metal to be analyzed. The shadow cast by the edge of the ribbon, and the diffracted beams due to its suitably oriented crystals are caught by a strip of photographic film wrapped on a cylinder, the axis of which coincides with the edge of the ribbon. The current through the x-ray tube is about 30 milliamperes, the potential across it about 30,000 volts. The radius of the film (sensitive side) is $r = 20.36$ cm. for the particular film-holders here used.

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[1] W. P. Davey, Opt. Soc. of Am. Jl., *5*, 479–493 (Nov., 1921).

The diffracted beams due to the individual crystals form full-sized images of the source,[1] which are separately distinguishable if the crystals are large enough, and which, when distinguishable, are more clearly defined the more homogeneous is the arrangement of atoms in the individual crystals. By keeping the sample at rest we thus gain information as to the dimensions of the crystals and their homogeneity. It should be mentioned that if the crystals are very large the images of the source are characteristically blurred at certain points, but this aperture effect is easily distinguishable from the general blurring of the spots due to imperfections in a smaller crystal. If the spots are numerous and intense, as in the present series of photographs, the more remote edges of the bands which they form on the photographic film are easily located within a couple of tenths of a millimeter, whether the individual spots are distinguishable or not.[2] The relative intensities of the bands will differ from the normal if the crystals are not oriented isotropically.[3] The distance from the edge of the shadow of the ribbon to the corresponding (more remote) edge of any band is $s = 2r\,\theta$, where θ is the grazing angle of incidence at which "reflection" takes place. The data, then, are the values of s, which range in these photographs from 6 to 30 cm. From these data the corresponding values of the perpendicular distance, d, between consecutive planes can be directly computed by the formula

$$d = \frac{\lambda}{2} \csc\left(\frac{s}{2r}\right),$$

where λ is the wave-length of the x-rays. In order to reduce the labor of computation by this formula a table was constructed giving $\log_{10} d$ to four decimals for the argument s at every 0.01 cm. from 2.50 cm. to 30.00 cm. The value of λ_2 for the longer wave-length component of the $K\alpha$ doublet, 0.71212×10^{8} cm., used in the construction of this table, was that given by Duane and Patterson.[4] The same table was used for the shorter wave-length component of the doublet, $\lambda_1 = 0.70783 \times 10^{-8}$ cm., when the doublet was resolved in the photographs, by subtracting a constant correction (0.0026) from the tabulated values of $\log_{10} d$.

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[1] L. W. McKeehan, Frank. Inst. Jl., *194* (1922).

[2] L. W. McKeehan, Frank. Inst. Jl., *193*, 231–242 (Feb., 1922).

[3] M. Polanyi, Zs. f. Phys., *7*, 149–180 (Nov., 1921).

[4] W. Duane, Nat. Res. Counc. Bull., *1*, 383–408 (Nov., 1920): W. Duane and R. A. Patterson, Nat. Acad. Sci. Proc., *8*, 95–90 (May 15, 1922).

The values of $\log_{10} d$ were computed in this way for every measured value of s. The indices of the corresponding planes (hkl) of the space-lattice were determined by inspection, the order and spacing of the bands being characteristic of the face-centered cubic space-lattice always found for the alloys here studied. The order of reflection is conveniently included in the indices h, k, l; *e.g.*, the second order from the planes (210) is indicated by the symbol (420). An auxiliary table was computed which gives $\log_{10} a/d$ for the first 54 bands of a simple cubic space-lattice, 22 of which, having h, k, l all even or all odd, are also found in the pattern for a face-centered cubic space-lattice. With this notation the usual formula[1] becomes

$$\frac{a}{d} = \sqrt{h^2 + k^2 + l^2}.$$

Adding the corresponding tabular numbers gives $\log_{10} a$ which should be the same for all the bands. Table I. shows how nearly this condition is satisfied. The mean value of $\log_{10} a$ was taken without weighting the separate values, since the more remote bands, on account of their relative faintness, have larger absolute errors in s and yield only slightly better values of a than do the more intense bands nearer the shadow of the specimen. The first band of the pattern, which is very intense, was sometimes rejected, however, if the values of s were inaccurate on account of a poorly defined shadow. A poorly defined shadow may be due either to use of too thin a sample or to over-exposure and partial reversal of the unshaded area.

ACCURACY.

An example of the data and calculations from a single film is given in Table I., which is self-explanatory. From calculations of this kind it is apparent that the probable error in the value of a from a single experiment is low; it is estimated at about 1 part in 500. Examination of different samples presumably alike showed however that these may differ in the value of a by as much as one per cent., although generally agreeing much closer. The widest variations occurred in condition R. Such variation is not surprising, since the value of a is really determined for a sample of metal which originally occupied only about one cubic millimeter in the ingot. In conditions RA and $RARA$ it is thought that the agreement of results for different samples justifies the statement that a is known to 1 part in 300. The compositions of the alloys, as given in Table I., are subject to errors which it is difficult to estimate.

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[1] A. W. Hull, Phys. Rev., (2), *10*, 661–696 (Dec., 1917).

TABLE I.

Material : Ag_2 Pd_3			Condition : RA		Film No. 298
Relative Intensity.	**Arc Length, s, in cm.**	**Due to $K\alpha_1$ or $K\alpha_2$.**	**log ($d \times 10^8$).**	**Miller Indices.**	**log ($a \times 10^8$).**
10.........	6.35	2	0.3603	111	0.5989
4.........	7.34	2	0.2979	200	0.5989
6.........	10.42	2	0.1482	220	0.5997
4.........	12.28	2	0.0787	311	0.5994
4.........	12.82	2	0.0606	222	0.6002
1.........	14.86	1	9.9963	400	0.5984
4.........	16.28	1	9.9586	331	0.5980
1.........	16.34	2	9.9597	331	0.5991
3.........	16.72	1	9.9477	420	0.5982
1.........	16.79	2	9.9486	420	0.5991
3.........	18.42	1	9.9083	422	0.5984
1.........	18.53	2	9.9085	422	0.5986
3.........	19.64	1	9.8825	$\binom{333}{511}$	0.5982
1.........	19.75	2	9.8828	$\binom{333}{511}$	0.5985
1.........	21.52	1	9.8462	440	0.5988
3.........	22.65	1	9.8262	531	0.5982
1.........	22.78	2	9.8266	531	0.5986
2.........	22.99	1	9.8205	$\binom{442}{600}$	0.5987
1.........	23.13	2	9.8207	$\binom{442}{600}$	0.5989
1.........	24.41	1	9.7974	620	0.5984
1.........	24.56	2	9.7977	620	0.5987
1.........	25.45	1	9.7816	533	0.5983
1.........	25.78	1	9.7768	622	0.5985

Mean value $\log(a \times 10^8) = 0.59873$,
$a = 3.969 \times 10^{-8}$ cm.

Even in the silver-palladium series an error as great as two or three per cent., which is improbably high, would not affect the conclusions drawn from the results. Evidence is given below for the belief that the composition was not appreciably altered by annealing.

NUMERICAL RESULTS.

Table II. contains the values of a determined from the photographs, together with the densities computed for the most homogeneous condition examined. The values of a as a function of the atomic per cent. of silver

Table II.

Formula.	Atomic % Ag.	Values of $a \times 10^8$.				Computed Density.	
		R.	RA.	RAR.	RARA.	RA.	RARA.
Ag......	100	4.080[1]	4.080[1]			10.49	
Ag_4Au...	80	4.104	4.081[2]			11.93	
Ag_3Au_2..	60	4.112	4.126[2]			13.50	
AgAu ...	50	4.082	4.088[2]			14.74	
Ag_2Au_3..	40	4.091	4.114			15.31	
Ag_3Au_7..	30	4.072	4.122[2]			16.06	
$AgAu_4$...	20	4.082	4.079[2]			17.44	
$AgAu_9$...	10	4.096	4.084[2]			18.24	
Au......	0	4.075	4.075[1]			19.24	
Ag......	100	4.080[1]	4.080[1]			10.49	
Ag_9Pd...	90	4.090	4.056	4.053	4.055		10.67
Ag_3Pd...	75	4.075	4.037	4.014	4.020		10.93
Ag_3Pd_2..	60	4.023	4.001	3.992	4.004		11.08
AgPd ...	50	4.006	3.982	3.974	3.975		11.28
Ag_2Pd_3..	40	4.004	3.969	3.949	3.956		11.43
$AgPd_3$...	25	3.949	3.945	3.952	3.934		11.60
$AgPd_9$...	10	3.924	3.921	3.930	3.909		11.81
Pd......	0	3.900[1]	3.900[1]			11.87	

are also presented graphically in Fig. 1, for the conditions used in the computation of densities. In determining the mass to be ascribed to each unit of structure the value $N = 6.0594 \times 10^{23}$, as given by Birge,[3] and the 1921 atomic weights: Ag, 107.88; Au, 197.2; Pd, 106.7, were chosen. The densities for the pure metals: Ag, 10.49; Au, 19.24; Pd, 11.87, are within the range of values usually obtained, those for gold and silver being very close to the accepted values. The density of palladium has been a matter of some doubt, values from 11.40 to 12.16 having been reported. It is thought that the value given here is the most accurate yet obtained.

The previously published values for the space-lattice parameters of these three metals are due to Vegard[4, 5] and Hull.[6] Vegard's data has been recomputed using $\lambda = 0.614 \times 10^{-8}$ cm. for the mean wave-length of the $K\alpha$ radiation of rhodium[7] and gives for silver, $a = 4.11 \times 10^{-8}$ cm., and for gold, $a = 4.09 \times 10^{-8}$ cm. both slightly higher than the values here found. Hull's value for palladium, $a = 3.95 \times 10^{-8}$ cm. is also higher than those here determined by the same method, but he states that the lines on the photograph which he obtained were rather faint and diffuse, which in the light of the present study suggests inhomogeneity. The presence of occluded hydrogen is a possible source of high values of a for this metal.[1]

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[1] Mean of several concordant values, including both conditions, *R* and *RA*.

[2] Mean of two concordant values.

[3] R. T. Birge, Phys. Rev. (2), *14*, 361–368 (1919).

[4] L. Vegard, Phil. Mag., (6), *31*, 83–88 (1916). Ag.

[5] L. Vegard, Phil. Mag., (6), *32*, 65–95 (1916). Au.

[6] A. W. Hull, Phys. Rev., (2), 17, 571–588 (1921).

[7] W. Duane, loc. cit.

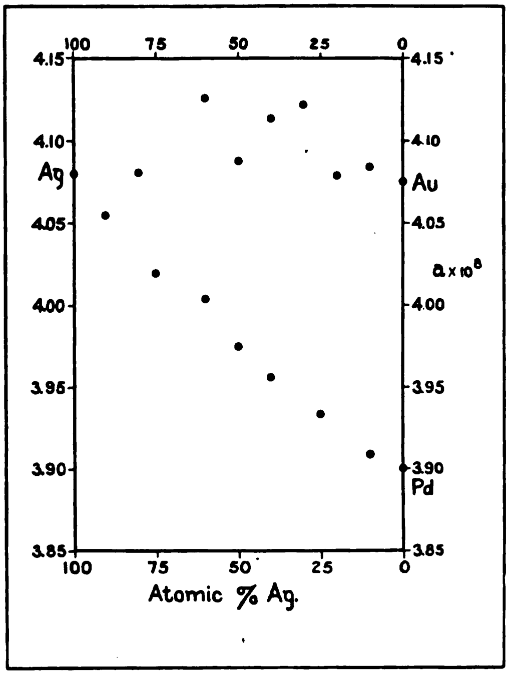

Fig. 1.

QUALITATIVE RESULTS.

The variation in the parameter of the space-lattice is, to a first approximation, a linear function of the atomic per cent. of either component. There is, however, a tendency for the chemically unlike components, Ag and Pd, to be packed more closely than this, and a tendency for the components of widely differing mass, Ag and Au, to be packed less closely when mixed in certain proportions. Whether the correlation between the observed facts and the properties to which attention is invited by this choice of words is accidental or not cannot be determined from such meagre data.

The abnormally high values of a obtained for Ag_3Au_2, Ag_2Au_3, Ag_3Au_7 suggest that Tammann[2] is right in concluding that in the face-centered cubic arrangement of atoms solid solutions of the compositions A_3B,

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[1] L. W. McKeehan, Amer. Phys. Soc. Washington Meeting, April, 1922.

[2] G. Tammann, Zs. f. anorg. u. allgem. Chem., *107*, 1–239 (1919).

AB, AB_3 are particularly symmetrical and homogeneous. The compositions of the abnormal members of the Ag-Au series fall between these points, and the alloy Ag-Au appears to be normal in its value of a. The high value for the alloy Ag_3Pd_2 may be due to the same effect, but the distance of this point from the smooth curve hardly exceeds the probable error in its position.

It should be mentioned that the method of measurement favors low values of a at the expense of high values, so that what is actually determined is the smallest a (and the largest density) possessed by a considerable fraction of the crystals. The sag in the Ag-Pd curve might accordingly be attributed to a greater variability in a for the intermediate members. The reason for preferring the hypothesis of increased interatomic attraction is that the bands are no broader and no more diffuse for those members of the series which give low values of a than for those which give high values, and no wider than the width of the sample requires.[1] In fact it is for the highest points on the Ag-Au curve that the difficulty of determining a is most increased by diffuseness in the bands. It is perhaps not irrelevant that the excess of the melting point over the annealing temperature is least in the Ag-Au series, so that diffusion may be more effective here than in the Ag-Pd series in preventing regular arrangements, even if once established, from persisting.

Recent work by Bain[2] indicates that the gradual variation in crystal structure here found occurs in other solid solution alloys. He also obtained evidence, in the case of Cu-Ni and Cu-Au alloys, of the special regularity of distribution at the critical compositions, A_3B and AB_3, predicted by Tammann.[3] No such evidence was obtained in this study, perhaps because Ag and Pd have atomic numbers too nearly equal to give a "reflection" due to their difference and because these particular compositions were missing from the Ag-Au series.

The high values of a frequently found in condition R cannot be the immediate result of the cold-working which the material has suffered, for they do not recur in condition RAR. They are accordingly ascribed to inhomogeneity, existing in the original ingot, in the arrangement of atoms within each crystal, which does not permit the interatomic forces between unlike atoms to have their maximum effect. It will not suffice to suppose that different crystals have different compositions, for, as stated above, those with the more compact arrangements would be the ones for which a would actually be measured. After annealing, which renders the individual crystals more homogeneous, as proven by the better definition of the diffracted images of the source, the effect of cold-working is only to break up the existing homogeneous space-lattice into smaller units, and to shear and displace these fragments into less isotropic arrangements. The increase in intercrystalline area, and in the number of atoms thereon which do not fit into both the adjacent space-lattices, would account for the normal decrease in average density associated with cold-working where there is much shear. If working is so severe, however, that the space-lattice is destroyed throughout considerable volumes it is possible that some segregation of the components can occur at the same time. Subsequent crystallization may then leave the components less well mixed than before this severe working, and thus give rise to crystals with abnormal values of a. Some of the Ag-Au alloys were rolled until brittle, and in this condition gave hardly any evidence of crystalline structure, which would represent the end of the first stage in the supposed process. As noted above, recrystallization is particularly slow in the case of Ag-Au alloys, so that no attempt was made to reëstablish the crystal structure in these samples, especially since, if the supposed segregation exists, heating in this condition would change the composition by evaporation of silver.

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[1] L. W. McKeehan, Frank. Inst. Jl., *193*, 231–242 (Feb., 1922).

[2] E. C. Bain, Min. and Met., Preprint 1139–N (Feb., 1922).

[3] G. Tammann, loc. cit.

The relative volatility of silver, mentioned in the last paragraph, is a possible source of error in the composition of the alloys, and this, particularly in the Ag-Pd series, might vitiate the conclusions as to the dependence of a upon the composition by changing the latter to an unknown extent. In order to estimate the possible effect of this volatility a sample of the alloy AgPd was repeatedly annealed at 870° C. for periods of 2 hours. No change in the value of a indicating a progressive change in composition could, however, be detected, so that any error due to this cause is negligible.

In conclusion I desire to express my indebtedness to my colleague Dr. E. F. Kingsbury, who placed at my disposal his first-hand knowledge of certain physical and chemical characteristics of the alloys here studied which suggested or confirmed the conclusions here presented.

RESEARCH LABORATORIES OF THE
AMERICAN TELEPHONE AND TELEGRAPH COMPANY AND THE
WESTERN ELECTRIC COMPANY, INCORPORATED, NEW YORK,
June 12, 1922.

DETECTING EFFICIENCY OF THE RESISTANCE-CAPACITY COUPLED AMPLIFIER TO 6,000 METERS.

By W. G. Brombacher.

Synopsis.

Detecting Efficiency and Current Amplification of the Resistance-capacity Coupled, Two-tube Amplifier.—Test of Hulburt's formula, giving a relation between detecting efficiency and the constants of the tubes and circuits, has been extended to 6,000 meters. The detecting efficiency is defined as b_0/A^2, where A and b_0 are the amplitudes, respectively, of the input grid potential and of the rectified component of the output plate current. It was found that (1) for any wave-length the relation between b_0 and A^2 is linear; (2) for constant wave-length, b_0/A^2 varied with the coupling capacity in accordance with the formula within about 10 per cent., being practically constant for capacities greater than 200 $\mu\mu F$; (3) for constant capacities, b_0/A^2 varied with wave-length for ranges 1,100 to 2,500 and 2,500 to 6,000 meters in fair agreement with the theoretical curve. The current amplification, $n = b_0/Eg^2$, where Eg is the amplitude of the potential impressed on the grid of the second tube, was found to be independent of the wave-length to 6,000 meters.

Plate current of vacuum tube (Radiatron UV 201) was found to be *sensitive to the external temperature.*

1. Introductory.

The detecting efficiency of the resistance-capacity coupled electron tube amplifier has been discussed by E. O. Hulburt.[1] He derived a formula which indicated the connection between it and the constants of the electron tubes and the coupling circuits. His experiments showed that the theoretical relation held in the region from 400 to 1,600 meters.

The detecting efficiency was defined by the relation $\lim\limits_{A\to 0} \dfrac{b_0}{A^2}$, in which A and b_0 are the amplitudes, respectively, of the input grid potential and of the rectified component of the output plate current.

Consider the high frequency amplifier of two tubes as shown in Fig. 1.

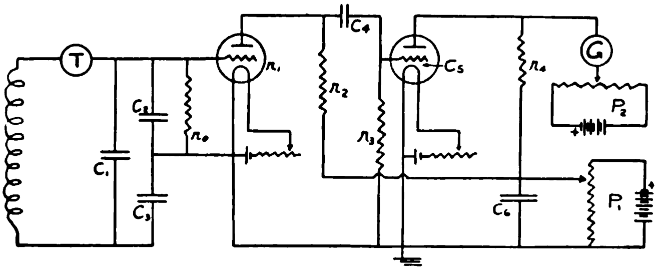

Fig. 1.

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[1] Phys. Rev., 18, 165, 1921.

For this type of amplifier Hulburt derived the following formula, subject to the conditions that there be no rectification in the first tube and no grid filament current in the second tube

$$\frac{b_0}{A^2} = nk^2g_1^2 \frac{\dfrac{(g_2g_3 - x_4x_5)^2 + [x_4(g_2 + g_3) + x_5g_2]^2}{(g_2g_3 - x_4x_5 + g_1g_3)^2 + [x_4(g_1 + g_2 + g_3) + x_5(g_1 + g_2)]^2}}{\left(g_2 + g_3 + \dfrac{x_5}{x_4}g_2\right)^2 + \left(x_5 - \dfrac{g_2g_3}{x_4}\right)^2} \tag{1}$$

in which A is the amplitude of the radio frequency potential impressed on the grid of the first tube, b_0 is the rectified component of the resulting radio frequency current in the plate circuit of the second tube; k is the amplification constant of the first tube. r_1 is the internal resistance of the first tube from filament to plate. C_5 is the filament-grid capacity of the second tube. Resistances r_2 and r_3 and capacity C_4 are as shown in Fig. 1.

Let $\omega/2\pi$ be the frequency of the impressed voltage.

Let

$$\frac{1}{r_1} = g_1, \qquad \omega C_4 = X_4,$$
$$\frac{1}{r_2} = g_2, \qquad \omega C_5 = X_5.$$
$$\frac{1}{r_3} = g_3,$$

One term has not been defined, which is

$$n \equiv \frac{b_0}{E_g^2},$$

where E_g is the amplitude of potential impressed on the grid of the second tube. n does not depend on the frequency of the impressed voltage. (See Fig. 6.)

Let

$$g_2g_3 - x_4x_5 = a,$$
$$x_4(g_2 + g_3) + x_5g_2 = b.$$

Then, more accurately, the formula may be written

$$\frac{b_0}{A^2} = nk^2g_1^2 \frac{\dfrac{a(a + g_1g_3) + b(b + x_4g_1 + x_5g_1)}{(a + g_1g_3)^2(b + x_4g_1 + x_5g_1)^2}}{\left(g_2 + g_3 + \dfrac{x_5}{x_4}g_2\right)^2 + \left(x_5 - \dfrac{g_2g_3}{x_4}\right)^2}. \tag{2}$$

It is to be noticed that this formula gives the detecting efficiency in terms of the constants of the electron tubes and the coupling circuits. Also Formula (1) is an approximation of (2), the use of which is justified under obvious conditions.

The object of this paper is to make the experimental measurements necessary in order to test Formula (1) for long wave-lengths, and to this end measurements were made from 1,000 to 6,200 meters.

2. Apparatus.

The apparatus consisted of a condenser potential divider, the amplifier and a D'Arsonval galvanometer. The arrangement is essentially that of Fig. 1. The potential divider consisted of the coil L, the Weston thermo-galvanometer T, and the condensers C_1, C_2 and C_3. This apparatus has been previously described by Hulburt and Breit.[1] The potential impressed on the grid of first tube may be found from

$$A = \frac{C_3 I}{\omega(C_1C_2 + C_1C_3 + C_2C_3)}, \tag{3}$$

in which I is the effective current measured by T. By coupling L to a suitable electron tube generating set, unmodulated high-frequency voltage of a small known amplitude and frequency was impressed on the grid of the first tube. The high-resistance leak r_0 was connected across C_2 to insure a definite value of the grid potential during the experiment. The effect of r_0 upon the impedance of C_2 was negligible because C_2 was large (either .05, .1, or .2 MF) and the frequencies used were of the order of 10^5.

The amplifier was a two-tube one with resistance capacity coupling. The tubes were General Electric Company tubes, Radiatron type UV 201; they were used with the filament current of .94 ampere and had a common plate voltage supply of 52.3 volts. Separate storage cells supplied each filament. The plate current was found to be sensitive to external temperature changes, an effect explained, perhaps, by the fluctuation in the amount of the absorbed gases in the glass walls of the tubes. It was therefore found necessary to enclose the electron tubes in covered cardboard tubes in order to keep their temperatures constant. The plate battery was shunted by a 1.75 MF condenser C_4. The resistance r_2 was 115×10^3 ohms and r_3 was 360×10^3 ohms. The resistances r_0, r_2 and r_3 were non-inductive, being of the type described by Hulburt.[2] These were found to give satisfactory service. The value of the resistance for high-frequency currents was assumed the same as that measured with direct current.

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[1] Phys. Rev., 16, 274, 1920.

[2] Loc. cit.

The change in the value of the rectified high-frequency component of the plate current of the second tube of the amplifier, designated by b_0, was measured by a D'Arsonval galvanometer, G, Fig. 1, connected across a resistance r_4 placed in the plate circuit. r_4 was 60,000 ohms. The galvanometer had a resistance of 9.0 ohms and a sensibility of 5.8×10^{-8} amperes per millimeter deflection on a scale 125 cms. distant. P_1 and P_2, Fig. 1, were potential dividers, P_1 serving to keep the plate voltage at the desired value, and P_2 to compensate for the potential drop in the resistance r_4 so that the galvanometer rested approximately at zero. When the grid voltage of the first tube was changed, a deflection of the galvanometer resulted which was proportional to the change in the rectified high-frequency component of the output plate current.

It was important that the filament currents remain constant. Any change in these currents resulted in a shift of the operating point of the tubes. The electron tubes were seasoned before every series of readings until a reasonably constant condition of filament current and electron emission was reached. In order to eliminate the error due to the usual slow drift of the galvanometer, the two zero readings were averaged. It was found that the grid leak r_0 gave a constant potential of nearly zero on the grid of the first tube when its value was 246×10^3 ohms. This value was not critical. For large values of r_0, the value of the grid potential shifted when it was necessary to vary the value of C_3. A Kolster decremeter, calibrated by the Bureau of Standards, was used to determine the wave-lengths of the high-frequency current.

3. VARIATION OF COUPLING CAPACITY.

The reading of the coupling condenser C_4 was varied at each reading, a number of input potentials were impressed on the grid of the first tube and the corresponding galvanometer deflections were noted. From the reading of T, the thermo-galvanometer, and a knowledge of the capacities C_1, C_2 and C_3, the amplitude of the change of the input grid voltage A was computed, using formula (3). Three sets of readings were taken, at wave-lengths 1016, 3070 and 6235 meters. The resulting curves with b_0 the ordinates and A^2 the abscissa, are shown in Figs. 2, 3 and 4. It can be seen that for each value of C_4 for all three wave-lengths the $b_0 - A^2$ curves are straight lines. This fact has been established by a large number of similar curves, not shown here. The curves for any one wave-length are plotted from data taken with the potential divider condensers C_2 and C_3 held constant. A change in the value of C_3 caused the curve for any particular value of C_4 to shift and also to change its slope. This is shown in Fig. 3 by the curve marked 628′. This fact

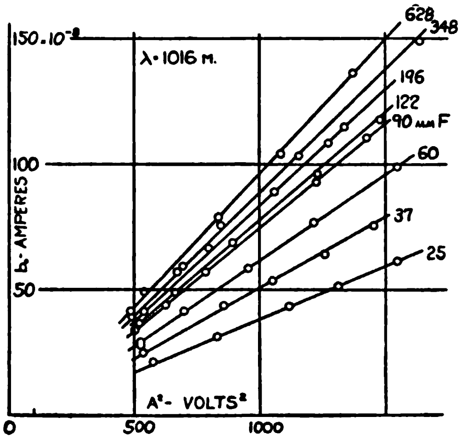

Fig. 2.

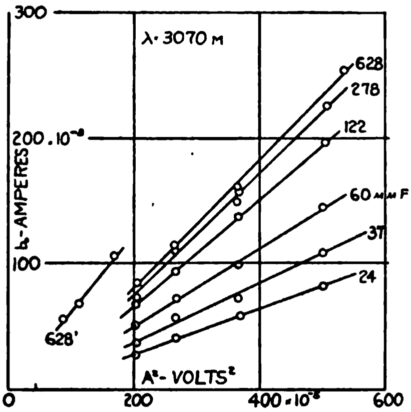

Fig. 3.

can be explained by a shift in the operating point of the first tube because of a shift in the normal value of the grid potential. r_0 had the value

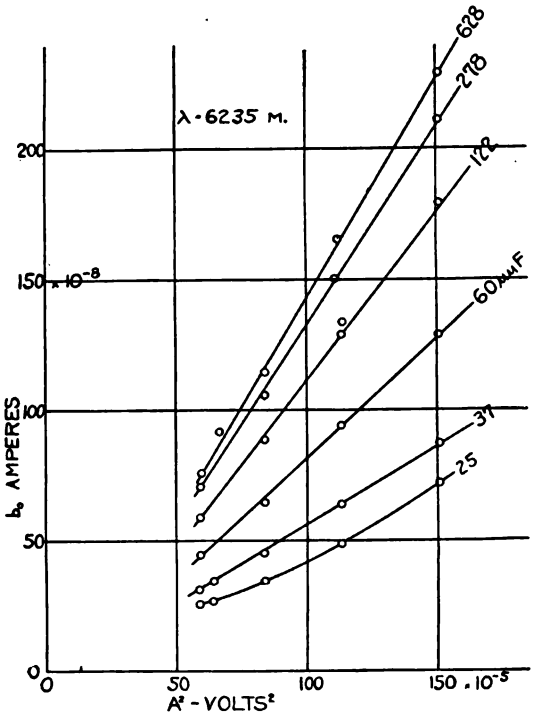

Fig. 4.

13×10^5 ohms during these readings. Another point of interest in these curves is that the straight lines do not pass through the origin, although within the limit of experimental error they pass through a common point on the A^2 axis. This seems to indicate a constant error in the determination of A^2 although a check up of the calibrations revealed no differences large enough for compensation. It is also of interest to notice that for each wave-length there is practically the same current range (b_0) but that there is a large range in the value of A^2; for 1016 meters, .006 to .015; for 3070 meters, .002 to .005 and for 6235 meters, .0006 to .0015 volt^2.

The main fact, however, remains that the straight lines were obtained, as is predicted by formula (1).

In order to further test formula (1) the slopes of the curves corresponding to each value of C_4 were determined and then plotted against values of C_4 for each of the three wave-lengths as shown in Fig. 5. That is, experimental values of b_0/A^2 are plotted against values of C_4. Then, from formula (1) the theoretical value was computed. Values of the constants not before given, r_1, the direct-current filament to plate resistance of the first tube, was 60×10^3 ohms; C_5, the filament-grid capacity of the second tube, was 18 MMF. This was measured in its socket and included the capacity of its lead wires, which were short, however. As neither n or k were determined experimentally, the computed curve was made to coincide with the experimental curve at C_4

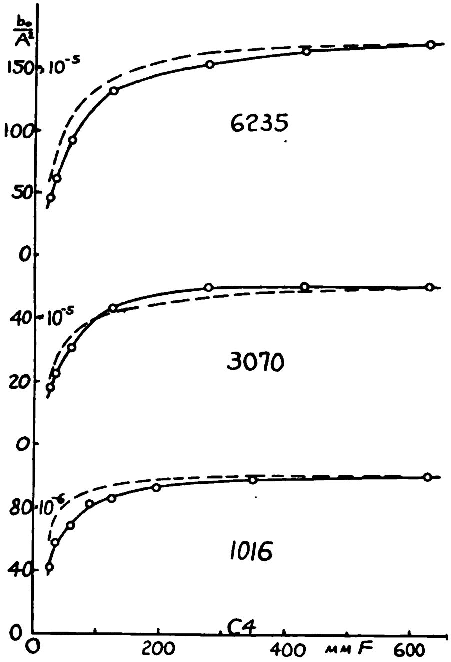

Fig. 5.

equal to 628 MMF. The computed curves are the broken lines. While the agreement between the experimental and computed curve is not exact, it is quite satisfactory, revealing no marked differences in behavior for two of the wave-lengths considered, while for wave-length 3,070 m. the agreement is good.

No change in the character of the computed curve was found whether formula (2) or its approximation (1) was used.

4. Variation of Wave-length.

The coupling capacity C_4 was kept at its maximum value of 628 MMF, r_2, r_3 and r_4 remained at their former values of 115×10^3, 360×10^3 and 60×10^3 ohms. A series of readings were taken so that the variation of detecting efficiency with wave-length could be determined. The experimental results are given in the full line curve of Fig. 6.

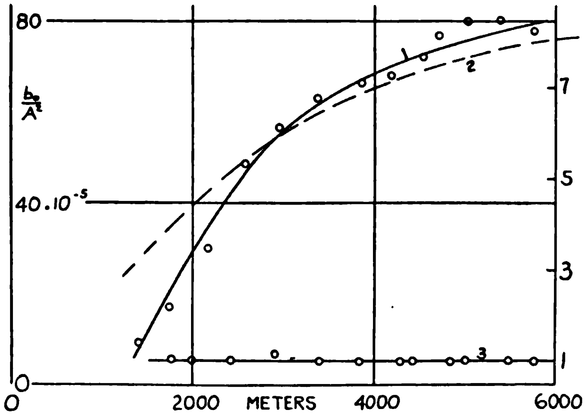

Fig. 6.

As the curve connecting the square of the input grid potential and the rectified component of output plate current does not pass through the origin, a series of readings was taken at each wave-length, a curve drawn and the slope determined. This slope is b_0/A^2. The experimental curves just mentioned were straight lines within experimental error.

In order to keep the grid potential of the first tube constant for the entire range of wave-lengths used, it was found necessary to fix its value near zero, which was done by making r_0 equal 246×10^3 ohms. This was tested by obtaining the deflection of the galvanometer when the condenser C_2 was short circuited, there being no high-frequency current in the input circuits. This test was made when the condensers C_1 and C_3 had values corresponding to the range of wave-lengths used. C_2 was 0.2 MMF throughout the run.

The computed curve, shown dotted in Fig. 6, was made to agree with the experimental curve in the neighborhood of 2900 meters. It was computed from formula (2), as the approximate formula (1) differed with it over the range of wave-lengths computed.

The agreement of the two curves is substantial above 2,500 meters, and, it is believed, would be even better, if the apparatus had been used with better control over the grid potentials. The poor agreement at lower wave-lengths is due to the difficulty of keeping conditions constant for the entire range of observations. An unpublished curve, detecting efficiency against wave-length, for the region between 2,500–1,100 meters gives a straight line of about the same slope as the theoretical curve. This is in agreement with the straight-line relation obtained by Hulburt between 600–1,600 meters. Thus, the simple theory underlying Hulburt's formula is in agreement with experiments thus far made.

It is seen that the detecting efficiency at higher wave-lengths (lower frequencies) becomes independent of the wave-length.

5. AMPLIFICATION.

It was necessary to test the independence of n with respect to wave-length. By definition

$$n = \frac{b_0}{E_g^2},$$

where b_0 is the rectified component of the output plate current and E_g is the amplitude of the potential variation on the grid of the second tube.

In order to measure n the input voltage was impressed directly on the second tube, the first tube being disconnected, and the output plate current was found for a series of wave-lengths. As before, sufficient observations were made for each wave-length so that a curve could be drawn and the slope determined. The slope was b_0/E_g^2. The curves so determined were straight lines. n was found to be sensibly constant for all wave-lengths as is shown in Curve 3, Fig. 6.

If the ordinate of Curve 1 be divided by the ordinate of Curve 3 at the same wave-length, both of Fig. 6, the quotient is the amplification of the current obtained by the use of the amplifying electron tube. That is, the quotient gives the number of times the rectified component of the plate current, b_0, is increased by the use of two tubes instead of one. The quotients, or current amplifications, are the ordinates on the right margin of Fig. 6. If telephones are used the sound intensity amplification is proportional to the square of these numbers.

This problem was suggested to me by Dr. E. O. Hulburt, now at the State University of Iowa, who derived the formula underlying the investigation.

JOHNS HOPKINS UNIVERSITY,
June, 1922.

THE THERMOELECTROMOTIVE FORCE OF COPPER-MANGANESE ALLOYS.

By Skezug Kimura and Zunehachi Isawa.

Synopsis.

Thermoelectromotive Force of Alloys of Copper with 5 to 23 Per Cent. Manganese for the Range 0° to 100° C.—The alloys were prepared from electrolytic copper and thermite manganese but contained as impurity about one fiftieth as much iron as manganese. The alloys were cast and then drawn to fine wires. After they had been annealed at 200° C. for 8 hours, the thermoelectromotive forces against fine pure copper wire were determined for various temperatures of the hot junction up to 100° C. The curves, as usual, correspond to the equation $E = \alpha t + \beta t^2$. For $t = 100°$ C., E is positive for all the alloys, especially if allowance is made for the effect of the iron content, though practically zero for alloys with less than 10 per cent. Mn. The alloys as cast and as drawn were more positive than after annealing. However, E showed negative values for the lower manganese alloys and for the lower temperatures, especially when the iron content was increased. In fact, though α is probably positive for all pure Cu-Mn alloys, *the effect of small percentages of iron*, carefully studied to 2 per cent. with a series of 30 alloys, was found to be to decrease α so that for 13 per cent. Mn and more than 0.50 per cent. Fe and for less than 11 per cent. Mn and more than 0.20 per cent. Fe, α is negative. On the other hand β is always positive but tends to decrease as the percentage of Mn is increased. Two alloys indicated that the *effect of 2 per cent. nickel* is to decrease α nearly as much as an equal amount of iron. *The effect of aluminum* seems to be the reverse but the five alloys tested did not give consistent results. *Ordinary manganese* contains just enough iron as impurity to make its E slightly negative at ordinary temperatures but adding 1 per cent. more iron, as suggested by Hunter and Bacon, would lower it too much.

Discussion of Electron Theory of Thermoelectromotive Force.—The electron theory does not account for the fact that E is positive rather than negative for Cu-Mn alloys against Cu, and that while Fe itself is positive against Cu its effect on E for these alloys is negative. It is suggested that the effect of atomic and molecular forces on the free electrons will have to be taken into account.

A KNOWLEDGE of the thermoelectromotive force of copper-manganese alloys and the way in which it is influenced by admixtures of other elements such as iron, nickel and aluminum is important because one or more of these alloys is widely used as standards for resistance. The data on this point being insufficient and somewhat contradictory, it was decided to study carefully the thermoelectromotive force of a large number of copper-manganese alloys.

In preparing the sample throughout this investigation electrolytic copper and thermit manganese were used and the metals were alloyed in Tammann tube furnaces. To protect from oxidation the necessary quantity of barium chloride was first melted in the furnaces and the metals to be alloyed were charged in convenient order into them. Then the melted alloys were poured into porcelain tube crucibles which had been preheated to about 500° C. and the ingots were slowly cooled. An ingot about 10 cms. long and 1.8 cms. thick thus obtained, was annealed at 800° C. for 30 min. and then drawn into a wire the diameter of which was about 5 mm. This wire was drawn cold in the usual manner. The diameter of the wire was reduced two numbers (B. & S.) with one drawing to gauge number 13 and after that was reduced only one number at each drawing. Until the diameter of the wire reached its final value, it was annealed several times for 8 hrs. in an oil bath at 200° C. All the specimens used for this investigation were in the form of wire (B. & S.).

After the specimen had been once more annealed at 200° C. for 8 hrs. in the oil bath, its mean thermoelectromotive force between 0° and 100° C. was measured against pure, fine copper wire. The hot junction of the thermoelement, consisting of the specimen and the pure copper wire, was kept in a hypsometer and the cold junction in an ice bath. Of course, the usual expression "mean thermoelectromotive force over a certain range of temperature" has no meaning for a thermoelement for which the thermoelectromotive force varies with the temperature so as to have a minimum or a maximum within the range. Some samples of copper-manganese alloys correspond to this case. For simplicity, however, the mean thermoelectromotive force was measured at first as usual. For the measurement of the thermoelectromotive force a Rap potentiometer made by Siemens and Halske and a d'Arsonval galvanometer made by Leeds and Northrup were used.

The results are summarized in Table I. and are also plotted in curve *E* of Fig. 1. For most of the specimens the quantity was insufficient to allow the small percentage of iron in them to be determined by analysis. But as all specimens were made from the same materials by the same treatment, the content of iron in them may be presumed to be of the same order as in the case of those specimens whose iron content could be determined by quantitative analysis.

From these results it will be seen that the mean thermoelectromotive force of copper-manganese alloys between 0° and 100° C. at least when the manganese content is between 5 and 25 per cent., is certainly positive against copper and that within the same limit of manganese content, the greater the proportion of manganese the greater is the thermoelectromotive force. Our results at this point confirm those of Feussner and Lindeck.[1] It is true that in Table I. there may be seen a few samples giving negative thermoelectromotive forces which casts a doubt on our conclusion. If Nos. 89, 102, 99 and 91 are considered, it will be noticed that even among samples with nearly the same percentage of manganese there are very large irregularities in the thermoelectromotive force. According to our experiments a small percentage of such impurities as iron, nickel and chromium can easily cause the lowering of the thermoelectromotive force. Judging from curve *E* of Fig. 1 drawn through all

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[1] Feussner and Lindeck, Abh. Phys. Tech. Reichsanstalt, 2, 515.

Table I.

Manganese Content and Mean Thermoelectromotive Force.

No. of Specimens.	Cu. (Per Cent.)	Mn. (Per Cent.)	Fe. (Per Cent.)	*E*/1° C. (Micro-V.)	*E'*/1° C. (Micro-V.)
84........	94.37	5.42	——	+ 0.03	+ 0.38
85........	92.74	6.97	0.133	− 0.04	+ 0.45
94........	91.85	8.04	——	− 0.01	+ 0.57
112........	90.29	9.52	——	+ 0.34	+ 1.24
100........	89.31	10.44	0.150	+ 0.02	+ 0.72
88........	89.26	10.45	0.150	+ 0.22	+ 1.04
89........	88.44	11.33	——	+ 0.38	+ 1.25
102........	88.40	11.46	0.170	+ 0.20	+ 1.02
99........	88.18	11.51	——	− 0.03	+ 0.61
91........	88.18	11.62	——	+ 0.12	+ 1.03
97........	87.30	12.40	——	+ 0.52	+ 1.48
101........	86.21	13.58	——	+ 0.50	+ 1.45
103........	86.07	13.65	——	+ 0.54	+ 1.50
90........	85.64	14.24	——	+ 0.65	+ 1.70
93........	83.50	16.29	0.290	+ 0.74	+ 1.85
95........	82.65	17.03	0.330	+ 0.78	+ 1.65
86........	82.11	17.58	——	+ 1.17	+ 2.10
96........	79.56	20.12	——	+ 1.73	+ 2.68
98........	77.05	22.52	——	+ 1.74	+ 2.58

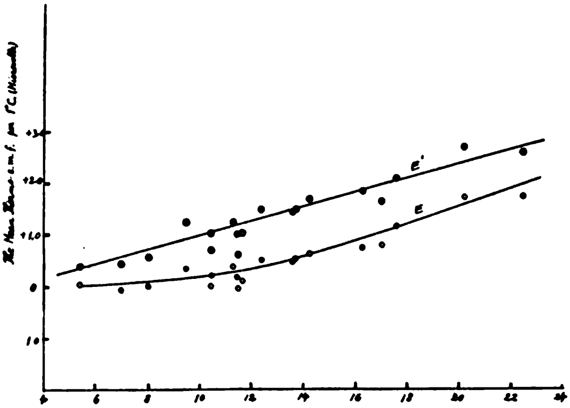

Fig 1.

Manganese content and mean thermoelectromotive force per 1° C. between 0° and 100° C. Curve *E'* for wires as drawn and curve *E* for wires after annealing.

the experimental points, No. 99 which gives a slight negative value may be considered an abnormal value due to the above cause. But this simple explanation is not sufficient to prove that the thermoelectromotive forces of the samples Nos. 89, 102 and 91 are nearer to the normal value than the thermoelectromotive force of No. 99, because if there are other reasons for raising the thermoelectromotive force of these samples, the opposite may equally well be concluded. For instance it was observed that the cast samples, even when they had been cooled at moderate speed, sometimes gave higher thermoelectromotive forces than those given by the same annealed samples. Curves I. and II. of Fig. 2 represent the thermoelectromotive force of a rod of copper-manganese alloy just cast and the same rod after annealing.

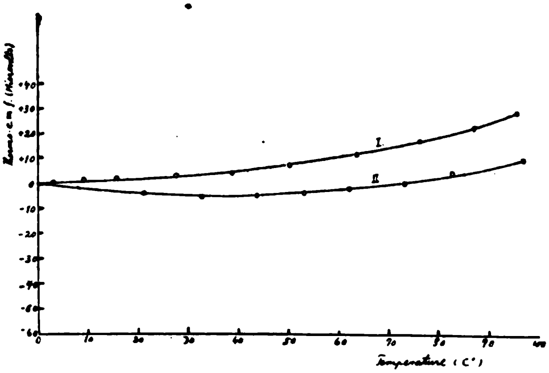

Fig. 2.

Thermoelectromotive forces of a copper-manganese alloy before and after annealing. Curve I. before annealing. Curve II. after annealing.

The effect of cold drawing must be taken into consideration as another cause of an increase in thermoelectromotive force. The value of the thermoelectromotive force represented by *E′* in Table I. and by *E′* in Fig. 1 are those obtained for samples just drawn, the corresponding values of the thermoelectromotive force for the same samples after annealing being represented by *E* in the same table and figure. It is, therefore, uncertain which value of the thermoelectromotive force, that of sample No. 99 or that of one of the samples Nos. 89, 102 and 91 is nearer the normal value. But if the state of the samples which gave the value of the thermoelectromotive force represented by curve *E* can be said to be normal, that is if the effect of the manufacturing process in our laboratory upon the majority of these samples can be said to be normal, then such samples as No. 99 can be considered abnormal. Iron may be considered as one of the causes of this abnormality.

THERMOELECTROMOTIVE FORCE PER UNIT DIFFERENCE IN TEMPERATURE.

In the previous section the mean thermoelectromotive force of copper-manganese alloys between 0° and 100° C. was found to be decisively positive against copper. Since the mean thermoelectromotive force is meaningless when the thermoelectromotive force per unit difference in temperature changes its sign between the two given limits of temperature, the variation of the thermoelectromotive force between 0° and 100° C. was studied for small temperature intervals. The hot junctions of the thermoelements were kept in an oil bath instead of in a hypsometer as in the preceding experiment. The oil bath was gradually heated by two incandescent lamps immersed in it and the temperature of the oil was kept uniform by means of a pump. The potentiometer was so adjusted that one division of the end dial just corresponded to one microvolt and a highly sensitive Thomson galvanometer was used for balancing.

The samples as before were in the form of wires and the results of their chemical analyses are shown in Table II. The iron in these samples is merely due to the impurity in the manganese. The results of the experiments on these samples have been plotted in Fig. 3. The values of α and β in the formula of the thermoelectromotive force, $E = \alpha t + \beta t^2$, have been calculated and plotted in Figs. 4, 5 and 6.[1] It is seen from these curves that α is negative for samples of lower manganese content and positive for those of higher manganese content, while β is always positive. The relation between α and the percentage of iron for various concentrations of manganese is brought out in Fig. 4 and the relation

TABLE II.

No. of Specimens.	Cu. (Per Cent.)	Mn. (Per Cent.)	Fe. (Per Cent.)	Ni. (Per Cent.)
184	94.318	5.198	0.1416	
185	94.833	5.002	0.1416	
186	91.541	7.920	0.1770	
187	91.541	8.003	0.1947	
188	88.196	11.575	0.1947	
189	89.182	10.147	0.1947	
190	87.103	12.292	0.2655	
191	86.842	12.540	0.2832	
192	83.774	15.840	0.3009	
193	82.996	16.253	0.3186	
195	86.337	11.673	0.168	1.830
197	85.556	11.424	0.186	2.616

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[1] Computed from the curves for $t = 40°$ and $t = 80°$ C.

between β and the concentration of iron in Fig. 5. The variation of α with the concentration of manganese for different percentages of iron in the alloy has been represented in Fig. 6.

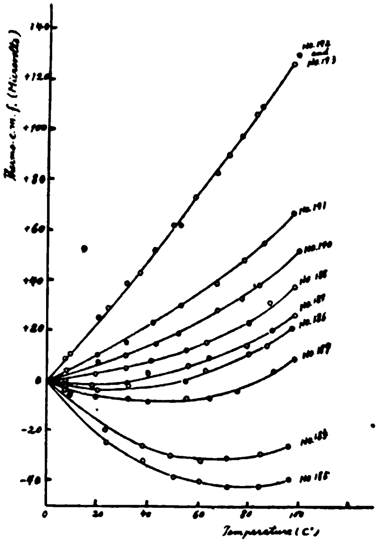

Fig. 3.
Manganese content and the temperature variation of the thermoelectromotive force as a function of the temperature of the hot junction.

In our opinion the difference between the curves in Fig. 3 is due to the fact that the effect of iron on the thermoelectromotive force varies widely with the proportions of copper and manganese. The samples Nos.

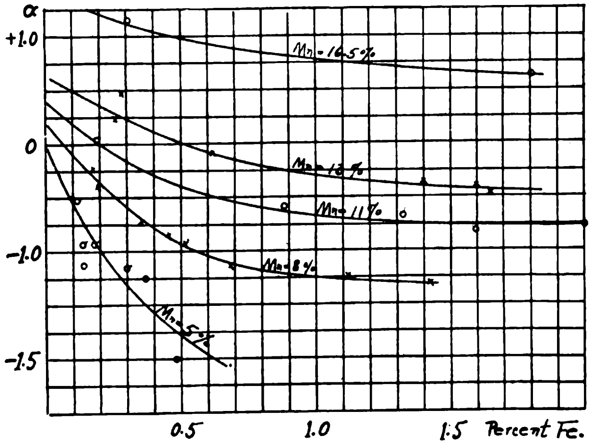

Fig. 4.
The variation of α in the equation, $E = \alpha t + \beta t^2$, as a function of the concentration of iron.

184 and 185 show exceptional negative thermoelectromotive forces and these results seem inconsistent with those obtained for sample No. 84 in Table I. Perhaps this discrepancy may also be attributed to the difference in the quantity of iron as an impurity. Though the above conclusion is very probable, further investigation will be necessary as to the thermoelectromotive forces of copper-manganese alloys in which the manganese content is less than about 6 per cent.

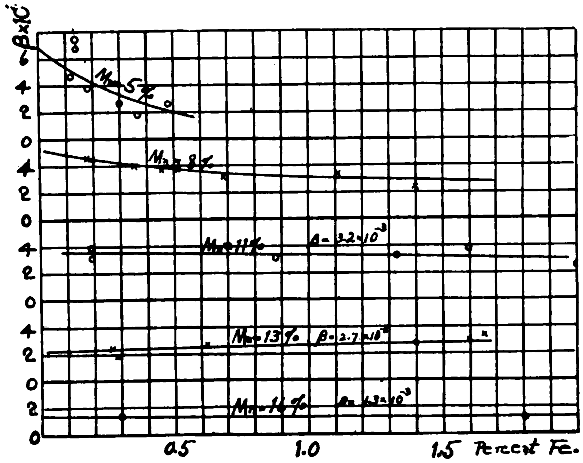

Fig. 5.

The variation of α in the equation, $E = \alpha t + \beta t^2$, as a function of the concentration of manganese.

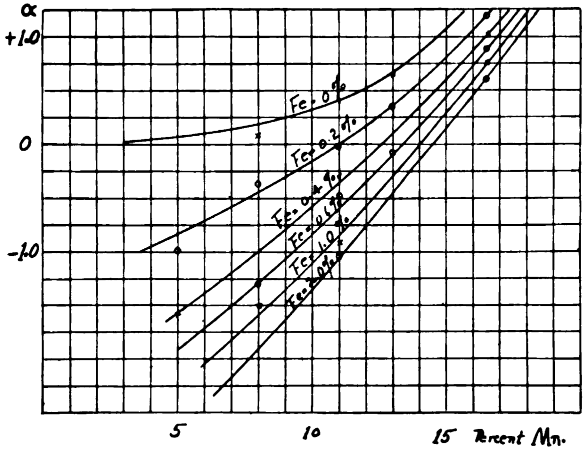

Fig. 6.

The variation of β in the equation, $E = \alpha t + \beta t^2$, as a function of the concentration of iron.

EFFECT OF NICKEL, IRON AND ALUMINUM ON THERMOELECTROMOTIVE FORCES OF COPPER-MANGANESE ALLOYS.

According to Feussner and Lindeck the positiveness of the sign of the thermoelectromotive force of copper-manganese alloys against copper can be annulled by the addition of a small quantity of nickel. For example, in a sample of about 12 per cent. manganese, about 2 per cent. nickel was suggested for this purpose.

It has already been seen that even though the mean thermoelectromotive force of copper-manganese alloys has a considerable positive value, dE/dt may not always be positive at ordinary temperatures. If attention is directed to the thermoelectromotive force of sample No. 189, it is seen that the mean thermoelectromotive force is about + 0.13 microvolt per degree Centigrade. But dE/dt for the same sample is negative for any temperature less than about 18° C. and it becomes zero at about 20° C. Thus it will be seen that copper-manganese alloys containing the same order of manganese as that in the ordinary manganin have a very small temperature coefficient of the thermoelectromotive force against copper at ordinary temperatures and that at lower temperature dE/dt becomes negative. If a small percentage of nickel is added to these samples, the thermoelectromotive force has a very large negative value at room temperature. This fact is clearly seen in samples of manganin wire on the market as well as those prepared in our laboratory (Fig. 7).

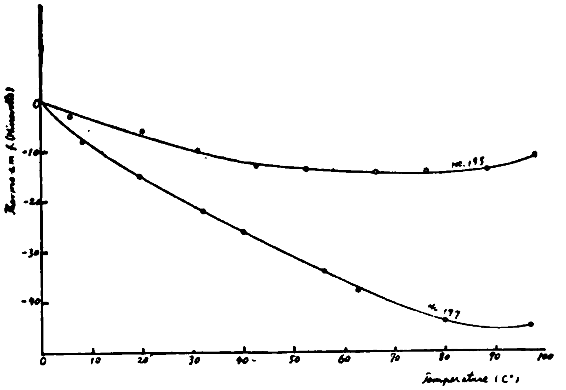

Fig. 7.

The effect of nickel on the thermoelectromotive force of a copper-manganese alloy containing about 11.5 per cent. manganese, as a function of the temperature of the hot junction.

It is thus seen that aside from its influence on the temperature coefficient of the resistance of manganin, the addition of nickel to manganin is not desirable where the manganin is to be used for standard resistances. Hence the idea of Feussner and Lindeck that nickel could be added to manganin to cancel the positiveness of the sign of the thermoelectromotive force, is not satisfactory because the effect is too large.

When manganin was first made by Feussner and Lindeck the iron content was perhaps nothing but impurity which came from the manganese. But it has been proposed by Hunter and Bacon that about one per cent. of iron should be added to manganin to improve the temperature coefficient of the resistance. Although there will be difference of opinion about this suggestion, it is important to investigate the effect of the presence of iron on the thermoelectromotive force of copper-manganese alloys, because iron is always present as an impurity in manganese. One example of the results of our experiments in this connection is given in Fig. 8. The results of the chemical analyses of these samples are contained in Tables II. and III.

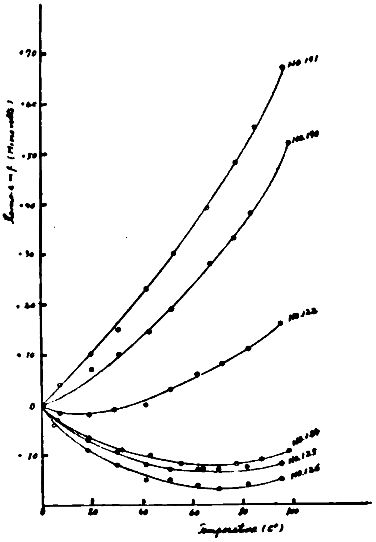

Fig. 8.

The effect of iron on the thermoelectromotive force of a copper-manganese alloy containing about 13 per cent. manganese as a function of the temperature of the hot junction.

Manganese Content and Mean Thermoelectromotive Force.

TABLE III.

Approx. Per Cent. Manganese.	No. of Specimen.	Copper, Per Cent.	Manganese, Per Cent.	Iron, Per Cent.
13............	122	85.573	13.430	0.6195
	124	85.330	12.877	1.3983
	125	85.073	13.117	1.5930
	126	85.330	12.877	1.6544

From these results it must be concluded that a small percentage of iron can cause a considerable lowering of the thermoelectromotive force of copper-manganese alloys and that its effect is of the order of that of nickel or sometimes rather greater than that of nickel. As already pointed out the presence of iron as an impurity in manganin is sufficient to lower the thermoelectromotive force of copper-manganese alloys and that the intentional addition of nickel is unnecessary. Furthermore, Hunter and Bacon's proposal to add about one per cent. of iron, is not desirable for the purpose of minimizing the thermoelectromotive force of copper-manganese alloys, because one per cent. of iron is far too much.

Recently in discussing a paper by Bash, Weimer has stated that an alloy of 84.2 per cent. copper, 11.5 per cent. manganese and 4.2 per cent. aluminum is an ideal material for resistance standards. He points out as the valuable properties of this alloy that its thermoelectromotive force against copper is about one tenth of that of manganin and that the constancy of its resistance seems to be quite good, while its mechanical properties are considerably better than those of manganin. According to our experiments aluminum affects copper-manganese alloys so as to make the thermoelectromotive force slightly more positive. Thus if aluminum is added there will be no need of any precaution against an excessive lowering of the thermoelectromotive force as in the case of the addition of nickel. The aluminum will make it less probable that the iron as an impurity will produce a large thermoelectromotive force. In this respect it is safer to add aluminum than to add nickel. But in our opinion the intentional addition of aluminum will also be unnecessary for the purpose of minimizing the thermoelectromotive force. Samples of this new alloy having various percentages of aluminum were prepared in our laboratory and their thermoelectromotive forces measured. But as our samples seem not to be homogeneous, a more detailed study of these alloys will be left for a later investigation.

RELATION OF RESULTS TO ELECTRON THEORY OF THERMOELECTROMOTIVE FORCES.

Certain solid solutions have negative thermoelectromotive forces against their solvent metals, while other solid solutions have positive thermoelectromotive forces. Any theory of thermoelectromotive force which makes it necessary for the thermoelectromotive force of solid solutions against their solvent metals to have one sign in all cases, is unable to explain such experimental facts as were obtained in this investigation. The present electron theory which can not in its present form account for such a reversal of sign, does not therefore offer a satisfactory explanation of these results. To make it possible for the electron theory to explain such results, it will be necessary to consider that atomic forces greatly affect the energy of free electrons and therefore the thermoelectromotive forces.

The Electrotechnical Laboratory,
Department of Communications,
Tôkyô.

NOTE ON OVERBLOWN PIPES.

PART I.

BY S. BHARGAVA AND R. N. GHOSH.

SYNOPSIS.

Minimum Pressures to Excite the Fundamental Note and Octave of a Pipe with Lip at Various Distances from the Edge.—It is well known that as the blowing pressure is increased first the fundamental is excited, then the octave appears, then after an interval of beating the octave alone is heard. With the pipe tested (fundamental pitch 490), as the lip distance was increased from 8 to 12 mm., the minimum pressures for the fundamental and octave, respectively, increased from 0.4 to 0.9 cm. and from 2 to 25 cm. of Hg.

Change of Pitch of a Pipe with Blowing Pressure.—This phenomenon is well known. For a particular pipe, studied with the help of phonodeik records, the fundamental pitch increased from 490 to 505 as the pressure was increased from 6 to 32 cm. of water. For 50 cm. of water the pitch (octave) was 1052.

THE experimental data necessary for working out the mathematical theory of the fluid motion near the mouth of an organ pipe seem to be wanting. Whatever accounts we have are scattered and incomplete. The present note describes a few quantitative results on (1) The variation of pitch with increase of pressure, (2) The minimum pressure necessary to excite the fundamental and the octave at various distances of the lip from the edge. The effect of the increase of the blowing pressure is to increase the pitch and the intensity, quantitative determinations of which are given in a paper in the PHYSICAL REVIEW.[1] The change in pitch with increase of pressure has been determined by the late Lord Rayleigh.[2] He employed resonators to determine the rise of pitch with increase of pressure. In order to be more accurate it was thought best to dispense with resonators and employ a photographic method for the determination of the pitch. For this purpose the record of the aërial vibration was obtained by a Phonodeik simultaneously with the trace of a vibrating fork on a sliding photographic plate. The frequency was determined by counting the number of waves. The following table shows a typical case.

The amount of variation in pitch is the same as observed by Lord Rayleigh. The important point to be noticed in the table below is the jumping of the pitch to the octave and, further, it must be noted that the frequency at 38 cm. of water is double that of the note just at the next lower pressure. At about 30 cm. of water the octave is clearly heard with the fundamental. With the rise of pressure the octave increases in prominence, and just before the note settles down to the octave only, there is beating as noticed by Raps,[1] Rayleigh and Lough.[2]

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[1] PHYSICAL REVIEW, Sept., 1920.

[2] Scientific Papers, Vol. 11, p. 92.

TABLE I.

Distance of Lip from Edge .8 cm.

Pressure in Water Column.	Frequency.
6 cm.	490 Fundamental
10 "	495
20 "	500
32 "	505
38 "	1050 Octave
50 "	1052

§ II. EXPERIMENTS WITH DIFFERENT POSITIONS OF LIP AND HIGH PRESSURES.

The lip was placed at different positions and made air tight. Compressed air was blown into the pipe, and the pressure near the mouth was recorded by a mercury manometer. It was found that the sequence of the phenomena is the same whatever be the position of the lip. The difference lies in the enormous pressure required to excite the pipe. We have observed in Table I. that the fundamental is elicited at a pressure of 6 cm. of water when the distance of the lip from the edge is about .8 cm. When the distance is 1.2 cm., the pressure necessary to excite the fundamental is 0.9 cm. of mercury (12.2 cm. of water). As the pressure is increased the pitch rises, but more slowly than the case when the lip was at .8 cm. from the edge. With the rise of pressure, the note develops its octave which is so strong that even an unaided ear cannot fail to detect it. As the pressure is further raised, the beat tone appears when on a slight increase of pressure the beat tone disappears, giving place to a steady octave. The necessary condition for obtaining the octave is the beat tone which is always obtained at a pressure depending upon the distance of the lip from the edge. Beyond the octave very little rise of pitch is obtained with increase of pressure. The addition of pressure increases the intensity considerably. In plate I. a few vibration curves which were obtained at high pressures are shown. Fig. 1 shows the fundamental, Figs. 2 and 3 show the gradual development of the octave clearly. Fig. 4 represents the octave which is more or less simple in character like the fundamental.

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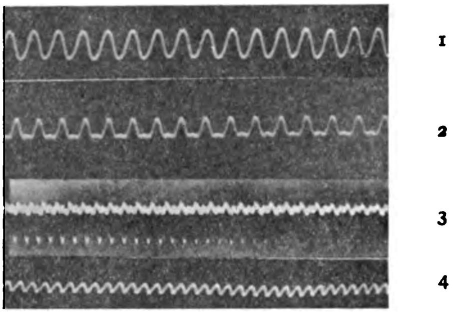
[1] Ann. der Phys., Vol. 1, p. 193.

[2] Phil. Mag., Jan., 1922, p. 72.



Figs. 1–4.

Fig. 5 shows the relation between the minimum pressures (ordinates in the figure) necessary to excite the fundamental at various positions of the lip. It will be observed that the minimum pressure increases slowly with increasing distance, then becomes rapid.

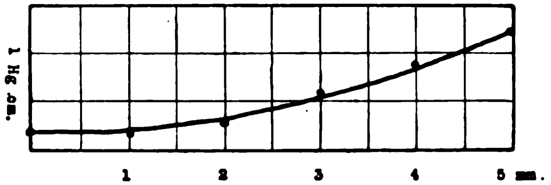


Fig. 5.
Origin representing .8 cm. from the edge.

Fig. 6 exhibits the relation between the pressure necessary to excite

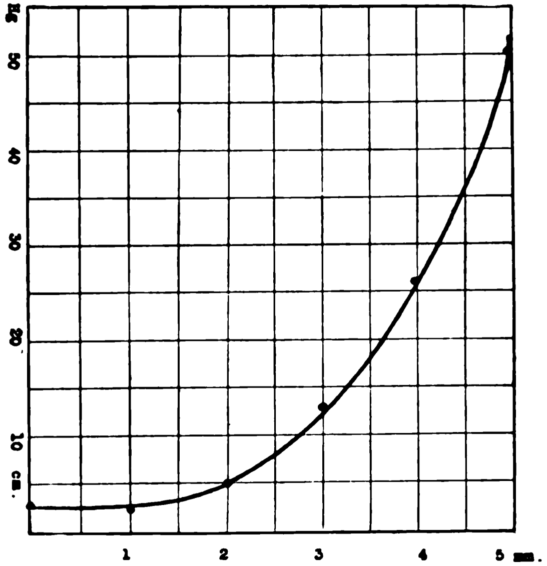


Fig. 6.
Distance of lip from the edge at the origin is .8 cm.

the octave at various positions of the lip. It is evident from the curve that the increase of pressure to change the note to the octave becomes greater as the lip distance increases. The curve is almost logarithmic to the distance axis.

§ III. Discussion of Results.

Since the rise of pitch with increase of pressure, the presence of the octave, and the beat tone, and finally the jumping to the octave, are quite general, *i.e.*, obtained at any position of the lip, it is evident that the hydrodynamical problem is quite definite. The fact that a certain minimum pressure is necessary to start the pipe, shows that the length of the air jet must be such as to allow it to flow past the edge. When the jet flows past the edge, it wafts to one side or the other delivering a puff at each journey. The maintenance is effected by the energy supplied by blowing. But this elementary view does not explain the gradual rise of pitch with increase of pressure. The effect of the increase of pressure is to produce a vortex motion whose effect is to diminish the effective inertia of the system, *i.e.*, the oscillating air jet, thus reducing the period. This qualitatively explains the rise of pitch. The presence of the octave and the beat tone can be explained on lines suggested by Lough.[1]

If we assume that the vortex motion has a certain natural period depending upon the pressure and decreasing with the increase of pressure then the phenomenon can be easily explained. Initially the period of the air jet is the same as that of the vortex pulsations. So that the two forces conspire, and produce the maximum effect. As the pressure rises, the period of the air jet decreases but more slowly than the pulsations, and in a short time they become discordant, when the fundamental is weakened. Finally the forces due to the pulsations excite in the pipe the next higher mode of vibration independently, *i.e.*, the octave, which becomes prominent, and the fundamental dies out. It will be observed from the above discussion that the pitch of the note on increase of pressure will jump to the octave of the note obtained at the next lower pressure.

Muir Central College,
Allahabad, India,
May, 1922.

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[1] Lough, loc. cit.

THE ENERGY LOSSES ACCOMPANYING IONIZATION AND RESONANCE IN MERCURY VAPOR.

BY JOHN A. ELDRIDGE.

SYNOPSIS.

Energy Losses Accompanying Radiation and Ionization in Mercury Vapor.—To make possible a *direct determination* of the distribution of electron energies after impact with vapor molecules, a special tube was constructed in which the usual grid was replaced by two diaphragms each pierced with only a single hole. These divide the tube into two chambers which can be maintained at different pressures, the one in which the collisions take place being kept at a sufficiently high pressure and the other, in which the energies of the electrons after the collisions are measured, at a very low pressure by the use of liquid air. The source of electrons was an oxide-coated platinum foil heated by radiation from a tungsten filament, and energy distribution curves were obtained for a given accelerating potential by recording the electron current as a function of the retarding potential. These curves show that below 4.9 volts the collisions are elastic but that at higher voltages energy losses of 4.9, 5.7 or 6.7 volts may occur. For example, with an accelerating field (corrected) of 9 volts, breaks occur for retarding potentials of about 2.3, 3.3 and 4.1 volts, the curve being approximately horizontal between breaks. When ionization is produced, however, the electron loses all its energy, even though this much exceeds the ionizing potential, 10.4 volts, and the electron freed by the ionization also seems to have practically no energy. The 6.7 volt type of radiating collision is not probable unless the energy of the colliding electron exceeds 8.5 volts, but it becomes far more prominent than the 4.9 volt type above 10 volts. *Comparison with spectroscopic and photoelectric data.* The observed radiating potentials correspond to the known absorption lines λλ 2536 (4.9 volts), 2330 (5.3), 2140 (5.9) and 1849 (6.7). Apparent discrepancies between these results and photoelectric data are discussed but the explanation is not yet clear.

WHEN, in 1913 and 1914, Franck and Hertz published the results of their investigation concerning the nature of electron collisions with gas molecules, there already existed a theory which accorded well with their observations, and their work and that of the many others that have worked in this field during the last decade has resulted in modifying, amplifying, but, to a surprising extent, in confirming the quantum theory as applied to atomic structure and radiation. This theory has directed much of the work in this field to the determination of the exact values of ionizing and radiating potentials, and in the case of the metallic vapors the result has almost invariably been an admirable check between these values and those predicted (by the quantum theory) from the spectral frequencies. It is surprising that comparatively little has been attempted in the way of giving precision to our conception of what actually takes place at these critical potentials. The most significant advance of this period was made when Davis and Goucher[1] showed that no ionization occurred at 4.9 volts in mercury. This changed and made much more interesting our picture of the phenomena, giving us two classes of critical potentials, the "resonating" and the ionizing potential. For the most part it has been so easy to fill in the hiatus left by experimentation with plausible extensions of the theory, that the gaps in the experimental evidence are not always apparent and yet a critical study of almost any of the investigations which have been published would show much that is not clear. Quantitative measurements are necessary before we can hope to solve all of these difficulties; yet some of the inconsistencies are so striking as to make us suspect some of the major tenets of our theory. Some of these difficulties formed the occasion for the present investigation, and as an introduction thereto it may be well to recall two recent studies of electronic collisions in mercury vapor.

In Fig. 1 is reproduced a curve, obtained by Mohler, Foote and Meggers,[2] and in Fig. 2 one by Franck and Einsporn.[3] The experimental arrangements of these observers were quite similar. The electron was accelerated from the hot cathode to a first grid, then entered a constant potential region where most of the collisions were made, and was then slightly retarded from a second grid to the plate. The current to the plate is plotted as ordinate, and the accelerating potential as abscissa. The curves are in a general way similar, the differences which exist being presumably due to the extreme purity of the mercury and constancy of experimental conditions in the work of Franck and Einsporn.

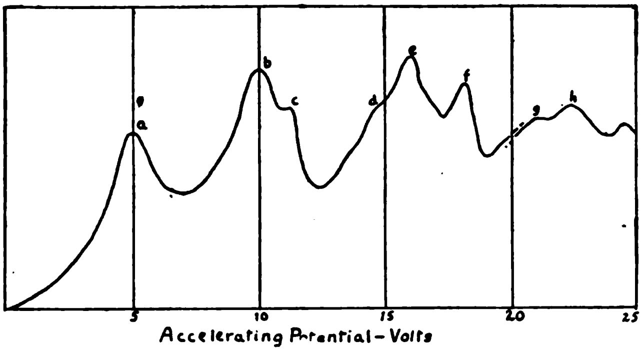

Fig. 1.

Mohler, Foote and Meggers, interpreting their results, point out that all peaks which occur are to be explained as due to combinations of collisions of the 4.9 volt and 6.7 volt type. The inflections at *a*, *b*, and *d* are due to successive collisions of the first type; *c*, *f*, and *i* to one of the first type combined with one or more of the second; *e* and *h* to two of the first and one or two of the second; and *g* is due to three of the first and one of the second. The new type of collision (involving an energy loss of 6.7 volts) corresponds to the λ 1849 line of mercury. This line is a prominent absorption line, and while it has never been observed spectroscopically below the ionization point, photoelectric evidence that it did indeed appear at 6.7 volts had been adduced by Goucher.

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[1] Phys. Rev., 10, p. 101 (1917).

[2] Journal Opt. Soc., 4, p. 369 (1920).

[3] Zeit. der Phys., 2, p. 18 (1920).

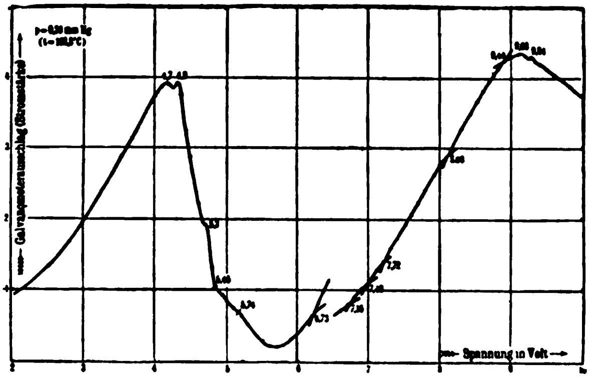

Fig. 2.

Figure 1 gives strong evidence for the existence of the second type of collision with the 6.7 volt energy loss. The peaks of the curve occur at voltages which check quite closely with those obtainable from combinations of multiples of 4.9 and 6.7 volts, and all such combinations are represented *excepting 6.7 volts itself and its multiples.*[1]

Curves similar to the above, showing two resonance potentials, were obtained for other metals of the second group of the periodic table: cadmium, zinc, magnesium, and calcium; but again, except in the case of calcium, no peak was found corresponding to a single collision of the second type. To account for this it was supposed that the inflection which should have occurred here was hidden by the overlapping effect of the first resonance point. This seems an unlikely explanation since later peaks, though equally close, are readily distinguishable. Moreover, as has been noted, just as there is no peak corresponding to a single 6.7-volt collision in Fig. 1, so there is none corresponding to any simple multiple of this. And yet this type of collision when it appears in combination with those of the 4.9-volt type gives very prominent peaks—peaks which are in fact more prominent than those corresponding to simple multiples of 4.9 volts, which beyond the second are quite weak.[1]

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[1] The agreement is not perfect. The interval between *b* and *c* and between *e* and *f* should be the same, *i.e.*, 1.8 volts, but the peak at *c* seems always to appear too soon.

There can be, however, little question of the essential rightness of the interpretation of the peaks which occur in Fig. 1, but an explanation is needed which will account for the absence of the others and for the relative magnitudes of those which do occur. The following hypothesis, at the time it occurred to the writer, seemed to be somewhat doubtful, and yet to be the only one which would bring consistency to the above seemingly inconsistent facts: At potentials slightly above 6.7 volts, collisions of the 6.7-volt type may be possible, but are very improbable as compared with those of the 4.9-volt type. As the potential is raised, these collisions become more and more probable, and at high voltages are more likely to occur than those of the 4.9-volt type. Single 6.7-volt collisions will take place on this hypothesis if an electron has a large enough kinetic energy—say 9 or 10 volts, but these will not involve a *total* energy loss and the electron will still reach the anode; at potentials just above 6.7 volts practically no collisions of this type will occur. The usual experiment indicates only the points at which inelastic collisions involving total or almost total energy losses begin to take place, and will, therefore, give no indication of a single 6.7-volt collision. Similarly, simple multiples of this type of collision, though often occurring, will not be indicated, because, to be indicated on the curve, the last collision must be by an electron with kinetic energy of just 6.7 volts, and such an electron will lose 4.9 rather than 6.7 volts of energy. The same hypothesis makes the first collision of an electron with high velocity more probably one involving a loss of 6.7 than of 4.9 volts. This would mean that peaks corresponding to pure multiples of 4.9 volts should be relatively weak at high voltages, and Fig. 1 shows that above 9.8 volts this is indeed the case.

There are other difficulties which occur in analyzing such a curve, but they will not be dwelt upon. The interpretation of the rise in current just before *c*, followed by the extremely sudden drop at *c*, is not clear to the writer. The rise is probably due to ionization, and our ignorance of what happens at ionization is fairly complete.

Turning to the curve of Franck and Einsporn, it is seen that in a general way it corresponds to the curve dicsussed above, but shows other weaker inflection points which are attributed to other types of inelastic collisions. In the earlier part of this very interesting paper, these writers show that a photoelectric effect occurs not only at 4.9 and 6.7 volts, but at many other potentials corresponding, through the quantum relations, to prominent lines in the mercury spectrum, a result in startling agreement with the Bohr conception of radiation. The curve showing the photoelectric current as a function of the accelerating voltage is not reproduced here.

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[1] I have obtained curves quite similar to Fig. 1, but because of the difficulties mentioned, I was not able to convince myself at the time that they were indeed due to 6.7 volt collisions.

The Bohr theory leads us to expect inelastic collisions at the "radiating" potentials indicated on the photoelectric curve, and Fig. 2 shows the inelastic collisions which were found to occur. As interpreted by Franck and Einsporn, this curve does show inelastic collisions at most of the radiating potentials. It is surprising however that no agreement was found between the magnitudes of the breaks in the two curves. In Fig. 2 we find the break at 4.9 volts of predominating importance, and this has no parallel in the photoelectric curves which indicated an emission of radiation at 4.9 volts of quite the same order of intensity as formed at 4.7, 5.3, 6.7, etc. The breaks indicated in Fig. 2 are certainly in most cases very weak, and correspond at times to inflections upwards and again to downward inflections in a manner which seems quite unaccountable. Inelastic collisions should always lead to downward inflections, according to the usual interpretation of such curves. The peak at 4.7 volts is more definite. The rise by which it is followed (just before 4.9) is unexpected, but can be explained if we assume that the 4.7 collisions cease when the potential slightly exceeds the critical value. Here, as elsewhere in the interpretation of the curves, we must suppose that Franck and Einsporn had a very small velocity distribution.

When the apparatus is suitably arranged (with high vapor pressure and no constant potential region), many repetitions of the 4.9-volt type of collision can readily be obtained which show little decrease in sharpness as the number increases. It is not difficult to understand the absence of the 6.7 type of collision from such a curve, since the electron probably never gets a velocity enough in excess of 4.9 volts to excite this radiation, but it would be thought that the critical voltages which lie nearer to 4.9 would be indicated by a rapid flattening of the peaks as the number increased.

Such are some of the questions which are left unanswered by recent experimentation in this field. The answer to many of them seemed to be obtainable by a method somewhat different from that hitherto employed.

As remarked above, the method developed by Franck and Hertz and quite generally used with modifications since then, measuring, as it does, the current to a retarding plate as a function of the accelerating voltage, is only competent to show the potentials at which *total* losses of energy *begin* to take place (complicated, above the ionization point, by the ionization current).[1] It seemed desirable to alter this method by keeping the accelerating potential constant and varying the retarding potential. For any given accelerating potential, it should be possible by such a method to measure the actual distribution of velocity which exists among the bombarding electrons after a considerable number of collisions with mercury vapor.

This method is a quite obvious deviation from the usual procedure, and was used by Franck and Hertz in their early work to show that the 4.9-volt maximum was due to an energy loss of the electron. Sponer,[2] in a paper which appeared after the present work was begun, has used a similar method and has made it yield very interesting results as to the probability of inelasticity at 4.7 and 4.9 volts. However, the tube used by these experimenters was of the usual filament-grid-plate design, and with such a tube the method is very greatly limited in its applicability. It is incapable of giving even approximate velocity distribution curves, and has so little resolution as to be probably quite useless in dealing with any velocity of more than a few volts.

For the purpose which the writer had in view, it was necessary to obtain the actual velocity distribution existing among the electrons in the mercury vapor. Therefore, an attempt was made to eliminate, so far as possible, the following obvious defects inherent in the grid type of tube, when used for such a purpose:

1. The electrons enter the retarding region with only one component of their velocities in the direction of the retarding field.
2. Collisions are made in this region, so that the electrons reach the plate only by diffusion. In the work of Sponer the free path was about half a millimeter.
3. Many electrons, though reaching the receiving plate, are reflected.
4. Electrons are reflected with loss of velocity from the grid.

The apparatus as finally developed is shown in Fig. 3. An earlier form of tube was used in taking some of the observations presented in this paper. It was the same in principle, but differed somewhat in design from the final form shown. These differences will be mentioned after describing the tube represented in Fig. 3.

The glass containing tube is shown shaded. *a* represents the cathode, an oxide-coated sheet of thin platinum supported on a small quartz tube and heated from above by a tungsten spiral. This furnishes a source of constant potential and one which is quite steady. *b* represents a nickel grid and wire cylinder; *c* shows a platinum cap, tightly fitting the inner tube and perforated by a small hole (0.6 mm. in diameter).

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[1] The recurrence of peaks gives, to be sure, evidence concerning the continuity of these collisions at higher velocities but these peaks are usually too complicated to be fully interpretable.

[2] Zeit. d. Phys., 7, p. 185 (1921).

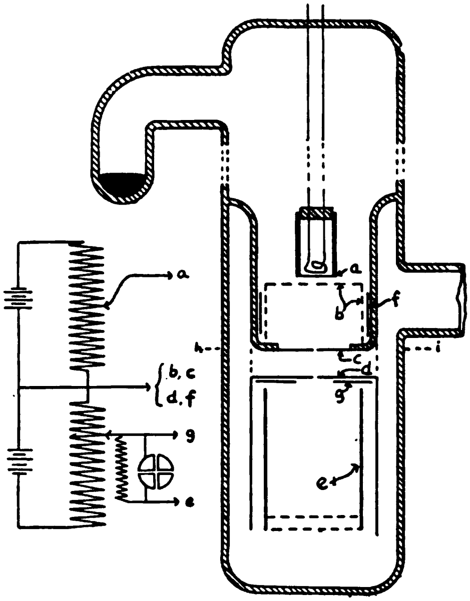

Fig. 3.

A nickel cylinder covered by a platinum disc with a similar perforation is shown at *d*, and *e* shows another nickel cylinder with its lower end covered by two layers of fine meshed nickel gauze and well insulated from other parts of the apparatus. To reduce electronic reflection, the inner walls of this cylinder are also lined with gauze. The distance between *c* and *d* is about 8 mm.

The tube is thus divided into two parts, communicating through the small hole *c*. During an experiment the upper part of the tube is electrically heated to any desired temperature (the mercury in the offset tube being somewhat underheated), and the lower part, below *h–i*, is immersed in liquid air. Under these circumstances, it is possible to maintain a high mercury pressure in the upper region, with a very much lower pressure in the region between *c* and *d*, and a good vacuum within the cylinder *e*. To avoid condensation of mercury on the nickel cylinders, the cylinder *d* was wrapped with nickel wire (not shown), and could be electrically heated while the tube was immersed in liquid air. A cylinder of thin aluminum sheet (not shown) was placed outside the nickel wire to reduce the radiation from the heated wire to the walls of the tube. A platinum cylinder is represented by *f*, placed behind the wire cylinder *b* and insulated from the hot, semi-conducting walls. This was used to take ionization curves in the usual fashion to check the behavior of the tube. *g* represents a nickel guard ring intended to be used to cut down the reflection of electrons from *e*, which electrons would have otherwise been attracted away from *e* by the field between *e* and *d*. The reflection was in fact small with this tube, and the ring had little effect.

All lettered parts had separate leads to the outside of the tube, but normally *b*, *c*, *d*, and *f* were maintained at the same potential. The electrical connections in such a case are shown in the figure. From *a* to *b* an accelerating field of any desired value is applied. The electrons enter the region below *b* with the velocity corresponding to this difference in potential, and collide with many mercury molecules here; some reach *c* and after a last collision pass through the small hole, and of these some enter the hole in *d*. A variable retarding difference of potential is established between *d* and *e*, and the current to *e* is measured as a function of this potential difference.

The earlier form of tube differed in design from that shown in Fig. 3 in that parts lettered *f* and *g* were missing, and a less direct method of eliminating the mercury vapor from the evacuated region was employed. In this case, instead of freezing the vapor out on the sides of the main tube, short side tubes were used, ending in mercury vapor traps. This tube probably gave a somewhat higher vapor pressure in *e* than did the later form shown.

An extremely small portion of the total current passes the two holes, and it is necessary to measure this current with an electrometer. A constant deflection method was used, using a shunting resistance of some 10,000 megohms of graphite on glass. This was kept dry over phosphorous pentoxide, and was very satisfactory, giving no evidence of polarization.[1]

The electrometer deflections were recorded in most cases photographically. This gave a continuous and rapid record of the current as the retarding potential was gradually increased. A Compton electrometer was used, with a period short enough to enable it to follow the impressed variations quite accurately.

The electrons passing through the perforations will reach the cylinder *e* and be measured as current so long as their velocity is greater than the retarding potential. The ordinate at any point on the current-retarding potential curve represents the number of electrons which had a kinetic energy greater than the retarding potential, or from the slope of the curve the number having any particular velocity is given. It is assumed that the electrons going through the holes are representative of those in the region *b*. If, then, it were possible to produce in this region electrons with kinetic energies of exactly 9 volts, the curve should be quite horizontal from 0 to 9 volts, and suddenly drop to zero. Or if half of these 9-volt electrons made collisions involving an energy loss of 4.9 volts, the curve would have a constant ordinate for retarding potentials from 0 to 4.1 volts, and then suddenly drop to a half value, which it would maintain until 9 volts. This illustrates the strong possibilities of the arrangement in resolving neighboring critical velocities, the resolution being only limited by the range of velocity distribution attainable.

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[1] In this method there is a slight correction to be made to the apparent potential of *e*, due to the *IR* drop in the shunting resistance, but this was only about 0.2 volt for a maximum deflection, and this correction has not been applied to the curves. Its effect will be appreciable only in estimating the distribution of velocities of emission which is in fact 0.1 or 0.2 volt less than that apparent from the curve.

In Fig. 7 the upper curve is a typical velocity distribution curve in vacuum (mercury free), taken with the tube illustrated in Fig. 3. The accelerating potential in this case was 12 volts. This curve shows a very satisfactory performance of the tube and a velocity distribution from the oxide-coated source which is mostly within a volt. The curve remains horizontal to 8 volts, then after a slight increase falls rapidly to zero, the slow electrons being lost in appreciable numbers at about 10 volts (which indicates a contact potential difference between *a* and *e* of 2 volts) and the fastest ones are lost when the potential is raised to 11 volts. The slight maximum at 9.5 volts is probably due to reflection of electrons from *e*. This reflection is less at low velocities, and consequently the number of electrons received and held by *e* is actually greater for high retarding potentials than for lower. There is every reason to believe that the drop in the curve does give very nearly the actual distribution of initial velocities.

CONDITIONS FOR THE OCCURRENCE OF 4.9-VOLT AND 6.7-VOLT COLLISIONS.

Figure 4 represents curves taken with the earlier form of tube. The mercury temperature was 140° C. in the cases of the upper two curves, and for the others 120° C., but the actual vapor pressures in *b* with this tube were somewhat less than the saturation pressures at these temperatures.[1] For each curve the accelerating potential (between *a* and *b*) is a constant, and its value corrected for contact difference between *a* and *b* is given for each curve; the uncorrected value is given in parenthesis.[2]

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[1] Owing to condensation on colder walls, which was not entirely avoided in this tube.

[2] The correction for contact difference between *a* and *b* was made by taking the usual resonance curves, measuring the current to *c*. The first peak occurred at 6 volts, instead

The curves were photographed with the current to *e* (ordinate) as a function of the retarding potential between *b* and *e*; in Fig. 4 the different curves have been so placed that the corresponding drops on different curves fall approximately above one another. The abscissa marked 0 represents then for each case the potential of the source, and the other abscissas give the potential of *e* relative to the source.

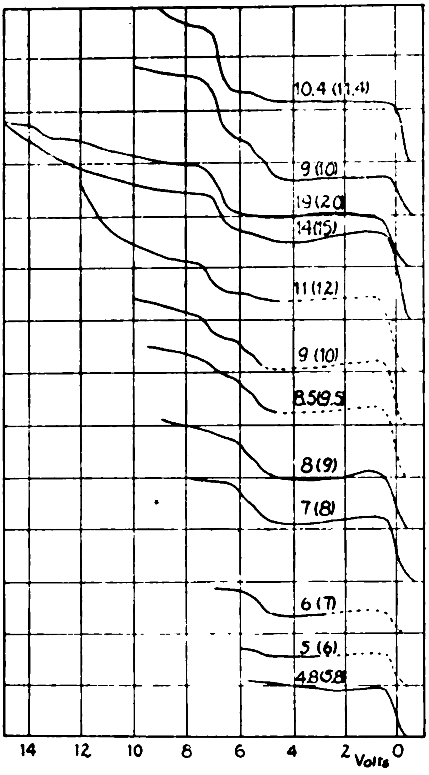

Fig. 4.

However, the meaning of the curves is most easily seen, if the scale of abscissas is for the present ignored and it is remembered that the left-hand end of any curve gives the current to *e* for no retarding potential between *b* and *e*.[1] From here, as we pass to the right, the retarding potential gradually increases, the vertical rulings giving this potential in two-volt intervals. For instance, the curve labeled 6 (7) is for electrons with a corrected velocity as they enter the region between *b* and *c* of 6 volts. As we proceed from left to right on this curve, we find the

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of 4.9, and ionization at 11.3 instead of 10.4, indicating a correction of one volt to be applied to the observed accelerating potentials.

[1] That is no apparent potential difference—there is a contact difference of potential.

current at first decreases slightly until the retarding potential is 1.3 volts, when it drops more rapidly to about half its former value. As the retarding potential is further increased, the current stays nearly constant (increasing slightly) until a retarding potential of 6.5 volts is reached, when it drops rapidly to zero. (The fact that it requires 6.5 volts to stop 6-volt electrons is due to a contact difference in potential between *b* and *e*.) Of the total number of electrons passing through the hole in *d*, we see that we continue to get about half, with retarding potentials as large as 6.5 volts; the other half were lost with a retarding potential some 4.9 volts less than this—this group then had given up 4.9 volts of their initial energy by collision. The energy losses which the electrons have suffered are to be determined then by counting back from the steepest part of the terminal drop at the right end of the curve to similar points on preceding drops. Since the terminal drops come at approximately zero on the scale of abscissas, these energy losses can be read directly from that scale.

The lowest curve was taken with an accelerating potential of 5.8 (corrected 4.8) volts, which had been observed to be just less than the potential at which inelastic collisions set in. It is seen that in general the curve remains horizontal until the retarding potential is enough to overcome the velocity given by the accelerating field—that is, there is here no indication of energy losses due to collisions. The slight drop which occurs at first in the curve and which is found at the beginning of all the curves is probably due to mercury vapor which it was impossible to completely eliminate from *e*. The slight rise which occurs just before the terminal drop has been accounted for as due to electron reflections from *e*. Such a curve gives the best direct evidence that we have of the elasticity of collisions below the resonating potential.

The next curve[1] with 5 (6) volts' accelerating potential was (for the fastest electrons) just above the resonating potential, and gives direct evidence of inelastic collisions involving an energy loss of approximately 4.9 volts. The slight drop at the left end of this curve is due to electrons suffering such collisions. The 6 (7)-volt curve also shows this same energy loss, in this case suffered by a much larger proportion of electrons. At all higher voltages a similar collision is evidenced. Beginning at 7 volts (corrected), however, there are indications of another type of collision with energy loss of 5.7 volts. And at 8.5 volts the expected collisions involving losses of 6.7 volts begin to occur, and become more pronounced at 9 volts. The next three curves are taken above the ionization point, and show the extreme importance of the 6.7-volt type of collision, the 4.9-volt and 5.7-volt drops having nearly disappeared. The 19-volt curve shows indications of an energy loss of 2 × 6.7 volts, corresponding to two of the more probable collisions.

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[1] Since the general shape of the curve was in some regions well known from previous work, and since it was desired to take these curves in as rapid succession as possible, the dashed portions were not actually observed.

The upper two curves of Fig. 4 were taken at higher vapor pressures, and show somewhat more pronounced drops at the critical potentials. The upper curve was taken just above the point at which ionization set in, and this shows that, at this voltage the 4.9 types of collision have become extremely improbable.

The 6.7-volt type of collision is then possible, and indeed above the ionization point is extremely probable as compared with the 4.9-volt collision. It does not seem to occur, however, in the cases of electrons with velocities only slightly in excess of 6.7 volts, but first occurs to an appreciable extent at 8.5 volts. The results are in exact accord with the hypothesis set forth earlier in the paper. That hypothesis was there seen to be required to explain the results of Mohler, Foote and Meggers; the present experiment is its direct proof. This completes the case for a 6.7-volt type of collision.

The distribution of velocities is more directly shown if the slope of the curves of Fig. 4 is taken and plotted as a function of the retarding potential. Such curves are given in Fig. 5. As in Fig. 4 the curves are super-

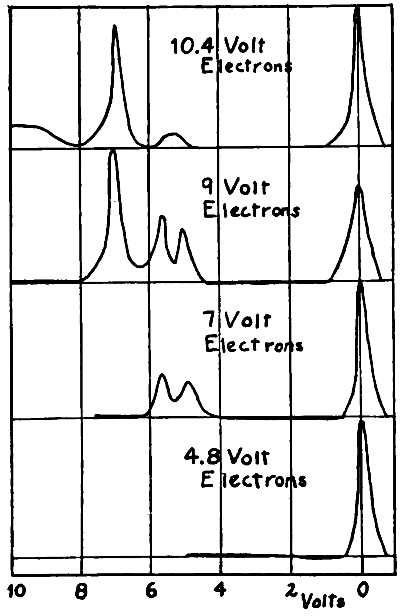

Fig. 5.

imposed and the scale of abscissas, instead of giving the retarding potential, gives directly the energy losses which have been suffered. The curves which are shown are for electrons which before collision had energies of 4.8, 7, 9, and 10.4 volts, respectively. The ordinate gives the relative number of electrons which have suffered energy losses corresponding to any particular value of the abscissa.[1] The negative values of the ordinates are of course meaningless, and are due, as mentioned above, to reflection from the walls of the receiving tube.

COMPARISON WITH SPECTROSCOPIC DATA.

Mohler, Foote and Meggers obtained resonance curves for cadmium, zinc, magnesium, and calcium similar to that for mercury. In each of these cases, then, there are two types of inelastic collision, and in the cases of the first three metals their curves show that the conditions for the two types of inelastic collisions are similar to those which have been shown to exist for mecrury.

Corresponding to these types of inelastic collision, mercury, as is well known, has been found to give a single line spectrum λ 2536, which may be obtained with an impact potential of 5 volts. The line λ 1849 has never been observed below the ionization point, probably due to its strong absorption by the vapor. For three of the other metals both lines have been observed,[2] the line of shorter wave length first appearing in the case of zinc about 0.4 volt, in the case of cadmium about 0.7 volt, and in the case of magnesium 0.6 volt above the corresponding resonance potentials. This is in satisfactory agreement with the discovery of the second type of inelastic impact by Mohler, Foote and Meggers, and with the present investigation.

McLennan and Ireton have maintained that while the λ 2536 line is the more easily obtained by electronic bombardment, the series whose first member is λ 1849 is probably the one which corresponds to some very simple type of electronic vibration within the atom, and is more fundamental in character. This view is in accord with the present results which show that though the longer wave length is more readily excited at low voltages, at higher voltages it becomes quite insignificant in comparison with the radiation of the second type.

The results of Davis and Goucher, who found indications of strong photoelectric emission at 6.7 volts, and the more recent results of Franck and Einsporn, who also detected this line among others, are not to be cleared up in this fashion. The methods employed by these writers gave the potentials at which the photoelectric emissions suddenly increased in value, and would be quite unable to detect the 6.7 type of emission if it did not begin until 8.5 volts.

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[1] While too much weight must not be laid upon the exact values of the ordinates the area under the peaks give the number of electrons which have suffered the corresponding energy losses.

[2] McLennan & Ireton, Phil. Mag., 36, p. 461 (1918); McLennan, Proc. Roy. Soc. A., 92, p. 574 (1916); Mohler, Foote & Meggers, Jour. Opt. Soc., 4, p. 364 (1920).

In Goucher's curves we find a photoelectric effect beginning at 4.9 volts, which increases several fold between 6 and 7 volts, and a second quite sudden increase in the current at 9.8 volts. Perhaps these curves are not to be quantitatively explained. It is certainly difficult to see why, if the larger part of the photoelectric current just below 9.8 volts was due to 6.7-volt collisions, as the curves are interpreted to mean, so large an increase in current takes place at 9.8 volts which corresponds to two collisions of the 4.9-volt type.

Franck and Einsporn find curves having the same general shape as those of Davis and Goucher, but with large numbers of discontinuities in shape. These discontinuities, interpreted as spectrum lines, agree wonderfully well with prominent mercury lines. These lines have never been spectroscopically observed under these conditions. There are several difficulties which are met when we try to account for the shape of this curve, and the lack of proportionality between the magnitude of the photoelectric effect and the probability of inelastic impact is hard to explain—yet the checks found with spectral data are so striking as to make it almost impossible to doubt the interpretation. There remains, however, much to be done in correlating spectroscopic, photoelectric, and inelastic impact data, and it is not strange if the present experiment does not seem compatible with the photoelectric data.

OTHER INELASTIC POTENTIALS.

Two features of the present type of tube seemed to make it admirably fitted to detect other forms of inelastic collisions than those of the 4.9- and 6.7-volt type.

In the first place, the resolving power of this arrangement should be greater than of that hitherto employed. In the usual form of curve, the suddenness of the drop at a critical potential largely depends upon what function the probability of inelastic collisions is of the velocity. These collisions do not take place immediately as the critical potential is reached, but in increasing numbers as it is exceeded. This has just been shown to be strikingly true in the case of 6.7-volt collisions and for a considerable range of voltage seems true for the collisions at 4.9 volts. And equally serious is the fact that the recovery from such potential is not immediate but distorts the curve seriously for several volts after the potential has been passed.

The resolving power of the present arrangement, on the other hand, is conditioned only by the velocity distribution of the source. The accelerating potential may be placed at a value which will give the maximum number of collisions of the type desired, and the retarding potential will detect the number of such collisions present, the drop being completed in a range equal to the initial distribution. This distribution is, it is true, a serious matter, but it is hoped that this can be cut down to a small fraction of its present value.

In the second place, such a tube integrates the effects of the different types of collision, and so even though the initial potentials were too close to be observed separately, the presence of such potentials would be indicated by a gradual drop in the curve in that region. Assuming a perfect tube, the curve will be horizontal, except at such potentials.

It has already been seen that an inelastic collision appears to take place, involving an energy loss of about 5.7 volts. There is little evidence of still other types of inelastic collision. The region about 6.7 volts has been investigated with some care but no consistent inflections were found which could be attributed to other lines. The gradual downward slope of the curve in this region probably should be attributed to the imperfections of the method, and probably to the presence of mercury vapor in the supposedly evacuated region.

The drop at 5.7 volts is too pronounced to be disregarded, and to some extent supports the conclusions of Franck and Einsporn, who, it has been remarked, found strong indications of spectral lines and weaker evidence of inelastic collisions at 5.45 and 5.7 volts.

Turning again to spectroscopic observations, it will be recalled that the lines λ 2536 and λ 1849, corresponding to 4.9 and 6.7 volts' impact velocity, have been found to be absorption lines as was to be expected from the theory. A group of absorption lines has also been observed in the neighborhood of 2330, and also a line at 2140 Ångstroms.[1] No absorption lines other than these have been observed by McLennan and Edwards above 1849 Ångstroms. These wave lengths correspond to electron energies of 5.3 and 5.9 volts, respectively, and agree with the present observation of an energy loss in the neighborhood of 5.7 volts.

Collateral evidence for the existence of an inelastic collision in this neighborhood is furnished by resonance potential curves obtained by the writer some time ago, and which at that time were quite inexplicable, as in many features they still are. These curves (Fig. 6) resemble in many details one published by Mohler, Foote and Meggers. The peak appearing at 9 volts corresopnds to one which they attributed tentatively to λ 1435.6 or λ 1402.7. Interestingly enough, this curve shows a pronounced maximum at 5.8 volts, which may be supposed to correspond to that placed at 5.7 volts from the velocity distribution curves.

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[1] Wood & Guthrie, Astro. Journ., 29, p. 211 (1909); McLennan & Edwards, Phil. Mag., 30, p. 295 (1915). McLennan & Edwards failed to find an absorption line at 2140, but it is not clear that this was not due to experimental difficulties.

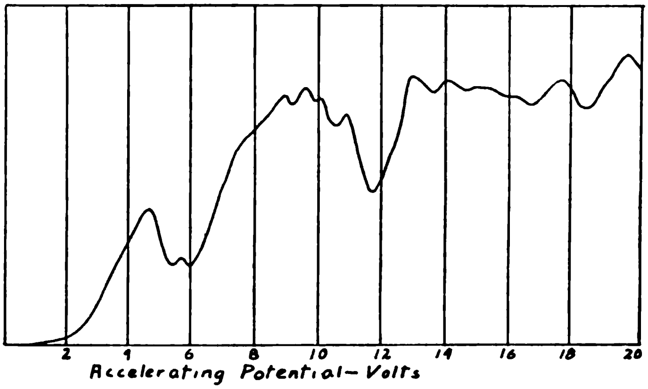

Fig. 6.

Ionization.

In contradiction to the generally accepted belief concerning the phenomena taking place at the ionization point, the curves of Fig. 4 give no indication of a loss of 10.4 volts of energy. No evidence for such a loss exists elsewhere.[1] The 10.4-volt inflection in the usual form of ionization curve which indicates ionization, does not reoccur at 20.8 volts, and it has been suggested elsewhere that this may mean that ionization does not involve a loss of a definite amount of energy in the same manner that a resonating collision does. The absence of the inflection at 20.8 volts cannot be considered conclusive evidence in the matter, however, as the experimental conditions make it quite likely that the double collisions necessary to give this inflection would be very improbable, and if occurring be difficult to detect.

It would be quite in accord with the Bohr theory if energy was absorbed above the ionization point in any amount above that just required for ionization. As long as the excited electron stays attached to the atom, its energy absorption is definitely fixed by the energy of an initial and a final position. But a free electron may have any velocity, and so it is quite in line with the theory that a 19-volt electron, say, should lose any part or all of its energy; if it lost all of its energy, the emitted electron would have 19 − 10.4 = 8.6 volts of energy after emission, and this effect would be indistinguishable from the case in which the primary electron lost 10.4 volts and the secondary electron had zero velocity; if it loses energy in any random amount over 10.4 volts, the emitted electron must, by this accepted theory, have enough to make the sum of the two remanent energies 8.6 volts. The first case leads us to expect a sudden drop in the curve at 10.4 volts from the terminus, and another at zero retarding potential. The second case would be shown by a curve which gradually drops in the region from zero to 8.6 volts retarding potentials, and at 8.6 volts (with a perfect tube) becomes horizontal, or at least has a change in slope at this point. Neither is in accord with the results of this experiment. It is true that, though the curves do not have the change in slope we should expect at the ionizing point on the curves, they do have a continued drop, which has been accounted for by the presence of mercury in the region from *c* to *e*. It is possible that this is rather the effect for which we are looking, the drop being continued below the ionizing point by a miscellany of critical potentials in that region which have not been resolved.

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[1] Except some recent results, as yet unpublished, of Noyes and Gibson, which seem to indicate that such a loss does occur.

To test this very important point, another tube was designed with a view to more immediate removal of the mercury which passes through the holes, to eliminate as far as possible the reflection of electrons, and to make it possible to check the behavior of the tube by taking conventional ionization curves. This is the tube which has been described (Fig. 3). The observations discussed in the above sections have all been checked with this tube.

It has been possible, under suitable conditions, with this tube to obtain curves which were practically horizontal except at the critical potentials. The upper curve of Fig. 7 is a typical velocity distribution

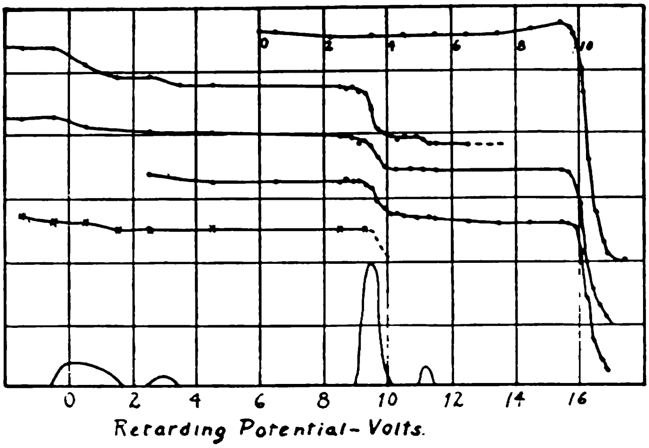

Fig. 7.

curve in vacuum. The other curves are for 16.5-volt electrons with the mercury at 90°. The cylinders *d* and *e* had been heated for some hours to drive out mercury as far as possible; during the observations they were cold.

By taking ionization curves by the usual method, measuring the current to *f*, it was ascertained that strong ionization was taking place under these conditions.

Several curves were taken with a view to detecting energy losses greater than 6.7 volts and these are given in the figure, with the current plotted against the retarding potential. From one of these curves (the upper one) the slopes have been taken and the lowest curve of the figure shows these slopes plotted as a function of the retarding potential. The curves all drop during the first volt; and two of the curves show another slight drop at about 3 volts. The current then remains constant until a retarding potential of about 9 volts is reached, when a drop occurs which is due to electrons which have made a 6.7-volt collision. A much smaller drop occurs at 11 volts, attributable to collisions of the 4.9-volt type. The drop which occurs in two of the curves at about 3 volts can be accounted for as due to two collisions of the 6.7-volt type. Between 3 and 9 volts the curves show no decrease in the current with increasing retarding potential and so are in contradiction both with the view that a loss of exactly 10.4 volts occurs at ionization and that a loss of energy in random amounts above this value can occur, with a transfer of the excess over that needed for ionization to the secondary electron. The first view would lead us to expect a sudden drop in the curve between 5.5 and 6.5 volts; from the second we would expect a gradual decrease in current in the region from 0 to 6 volts' retarding potential.

On all of the curves a slight drop is to be observed with small retarding potentials (1 volt) and the same effect is seen in curve 11 (12) of Fig. 4. This indicates a number of very slow electrons present after collision. It is not to be expected that these current drops will be large, because the slow electrons which are here being measured will quite likely combine with the positive ions present before they reach the hole in *c*. However, if *c*, *d*, and *e* are given a slight accelerating potential with respect to *b* (¼ volt), we should expect to get more of them, and in fact it is observed that under these conditions the current to *e* is greatly increased, perhaps twenty-fold. The current is reduced to its normal value, unless *e* is slightly accelerating. Such a phenomenon is only to be observed with accelerating potentials sufficient for ionization. This shows that there are indeed present at ionization a large number of electrons with zero velocity. Whether such electrons are the primary ones from the cathode, or those released at ionization, cannot be directly determined. However, since Fig. 7 shows that a total loss is the only loss greater than 6.7 volts which occurs, we may suppose that both primary and secondary electrons are represented in this group; that is, that after an ionizing collision, both primary and secondary electrons have zero velocity.

This conclusion seems to disagree with the Bohr theory, but perhaps this disagreement is not insuperable. Immediately after the removal of an electron from the atom it is conceivable that the remaining electrons do not have stable configurations and are quite easily displaced. Possibly after the electron strikes the atom and removes one electron, it may use its remaining energy in displacing other electrons in the now less stable ion. If the conclusion drawn from the experiment is to be accepted as valid, by some such picture as this it is possible to remove the discord with the Bohr theory.

Professor Wood [1] has found that above the limit of the principal series, the light absorption of a vapor becomes continuous. Such light should produce ionization, and this has indeed been shown to be the case in an investigation which has just been completed by R. C. Williamson. This continuous absorption of light for frequencies greater than the limit of the principal series presents an obvious parallel to the continuous absorption of energy of the electron when its energy is above the ionizing potential. It is a very interesting question whether the emitted electron in this photoelectric ionization has an energy at emission corresponding through the $h\nu$ relation to the amount by which the frequency of absorbed light exceeds the limiting frequency of the principal series. Such has been our general view, but if the parallel with the present results is perfect, these emitted electrons should have a zero velocity.

CONCLUSIONS.

The principal results which have been obtained from an examination of the residual energies after collisions of electrons in mercury vapor are:

1. The discovery by Mohler, Foote and Meggers of a resonance potential involving an energy loss of 6.7 volts has been confirmed. It has been shown that while this collision does not occur below 8.5 volts, at voltages above the ionizing point, this type of collision attains overwhelming importance in comparison with the collisions of the 4.9-volt type.

2. It is probable that inelastic collisions involving an energy loss of about 5.7 volts also occur, checking, to this extent, with the conclusions of Franck and Einsporn. The absorption lines which have been found

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[1] Phil. Mag., 18, p. 531 (1909).

in the spectrum of mercury support this view. Inelastic collisions corresponding to the other photoelectric lines of Franck and Einsporn have not been found.

3. At ionization the electron loses its total energy, even though this much exceeds the ionizing potential. The electron which is the product of the ionization seems likewise to have a negligible energy.

University of Wisconsin.

ELECTRICAL CONDUCTION ACROSS MINUTE AIR-GAPS.

By James W. Broxon.

SYNOPSIS.

Electrical Conduction across Minute Air-gaps.—As some results obtained by R. W. Wood are at variance with those of other observers, further experiments seemed desirable in which the separation of the metallic electrodes was determined optically. Therefore, two optical surfaces of nearly the same curvature were made conducting by depositing gold upon them by cathode discharge and were supported so as to be nearly in contact. Then, as the upper one was semi-transparent, the distance apart was determined by the interference rings produced by light of wave-length 0.546 μ. Using voltages of from 1.5 to 60, the minimum distance at which no conduction took place and the maximum distance at which conduction occurred were observed. Both these distances varied from less than a wave-length to several wave-lengths. In some cases the resistance of the gap during conduction was measured; it was found to obey Ohm's law and to be unaffected by radiation from 3 mg. of radium. The results suggest that the conduction was due to small projections from the electrodes or to dust particles. No disruptive discharge took place even when the potential gradient rose to 640,000 volts/cm., probably because the potential was less than the minimum which previous researches had indicated is necessary.

Existence of electron atmospheres at metallic surfaces, which was suggested by R. W. Wood to explain his experiments, seems very doubtful in view of the above results. At any rate, the atmosphere cannot extend more than one fourth wave-length or 0.14 μ beyond the molecular surfaces of the gold electrodes.

SOME time ago R. W. Wood [1] performed experiments which provided strong evidence of the existence of a medium, presumably an atmosphere of free electrons, capable of carrying electric currents between differences of potential of the order of one volt and extending beyond the molecular surface of a metal through a distance as great as thirty wave-lengths of sodium light. Not only were these results at variance with those of previous experimenters with small gaps (Carr,[2] Shaw,[3] Almy,[4] Williams,[5] etc. . . .) who found evidence that as a gap in an electric circuit is made very small there exists a minimum potential of the order of 350 volts which can cause a current to flow without actual contact, but Brown,[6] Englund,[7] and Householder[8] have since

[1] Phil. Mag. (6), 24, p. 316, 1912; R. W. Wood.

[2] Proc. Roy. Soc., LXXI., p. 374, 1903; W. R. Carr.

[3] Proc. Roy. Soc., LXXIII., p. 337, 1904; P. E. Shaw.

[4] Phil. Mag. (6), 16, p. 456, 1908; J. E. Almy.

[5] Phys. Rev., 31, p. 216, 1910; E. H. Williams.

[6] Phys. Rev. (2), 2, p. 314, 1913; F. C. Brown.

[7] Phil. Mag. (6), 27, p. 457, 1914; C. R. Englund.

[8] Phys. Rev. (2), 4, p. 47, 1914; F. F. Householder.

performed experiments dealing directly with the question and have secured negative results. It is important to observe, however, that in practically every instance the point of actual molecular contact (if one may say that) was established by electrical means, thus eliminating the true field of experimentation, for by this means it could only be determined that a continuous circuit, perhaps partially composed of an atmosphere of free electrons, had been established. This objection can not be offered against the work of Brown and Householder, but in the one case perfect insulation could not be obtained across a gap of less than nine wave-lengths, and in the other the actual areas of the opposed electrodes were exceedingly small, and no statement was made concerning the precautions taken to insure conductivity at all parts of the circuit other than the one under investigation.

Because of these considerations, it was suggested by Dr. W. F. G. Swann that the problem be investigated by a method which should reproduce as nearly as possible the conditions under which Wood found the effect most noticeable and which should at the same time eliminate difficulties involved in other methods used. The writer was able to do this in the following manner:

Care was taken to select a double-convex and a double-concave lens such that a very regular series of Newton's rings could be secured at whatever place the lenses were brought into contact. After a heavier ring had been deposited about its edge, one surface of each lens was then completely covered with a deposit of gold thrown down in a vacuum. A concave surface, of about 206 cm. radius of curvature and 3 cm. diameter, was covered with a film rather heavier than that known as semi-transparent, while a convex surface of about 127.5 cm. radius of curvature and 5 cm. diameter was covered with a film which was quite transparent.

A partial cross-sectional diagram of the apparatus made to hold the electrodes and to adjust the extent of their separation is shown in Fig. 1. The base of the instrument consisted of two brass rings about 4 mm. thick and with external diameters of 10 cm., held rigidly separated at a distance of 2.5 cm. by stout brass rods. The upper surface of the second ring was made with a raised collar about its inner circumference, the top of this being cut down until the remaining ledge supported the concave lens with its gilded surface well above any portion of the ring. At one place an incision was made in the collar to enable a small clamp, fastened to the lower side of the second ring and extending up along the cylindrical side of the lens, to hold a small piece of tin foil tightly against that side without exposing any metal at an altitude as great as that of the upper surface of the lens.

The convex lens was held similarly in a third ring with its gilded surface down, the diameter of the lens being sufficiently large that its supporting clamps were further separated from the second ring than was the upper film from the lower. The third ring was supported above and insulated from the rest of the instrument by brass rods which turned freely in the base and passed through threaded bone plates fastened to the ring. Adjustments were made either by heating the rods last mentioned or by turning them. While backlash was largely eliminated by insulated spiral springs, there was still sufficient freedom to enable the films to be brought into contact at any point desired.

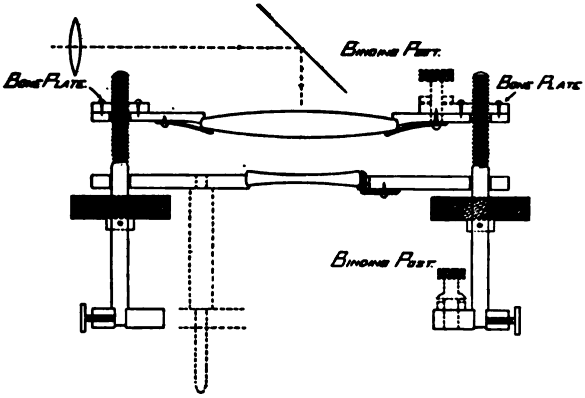

Fig. 1.

By means of a small plate of glass placed in a frame at an angle of 45 degrees to the planes of the rings, the green light from a mercury arc lamp was reflected against the lenses so that a system of Newton's rings was formed by reflection from the two gold films. In effect, then, two sections of very smooth thin spherical gold shells could be made to approach each other in a uniform manner. The center of the system of rings formed was observed through a traveling microscope between parallel hairs. Metallic contact was taken as occurring when the center of the system remained light and spread out over the field when greater pressure was exerted upon the lenses. As the thumbscrews were turned in a direction which would separate the films, each change in the center of the system from light to dark or from dark to light indicated an increase of one fourth wave-length between the points on the films nearest contact. The monochromatic filtered line used was .546 μ. Future reference to "wave-length" will be taken as indicating this distance.

The apparatus holding the films was first connected as the unknown resistance in a Wheatstone net with a very sensitive galvanometer, and the resistance of the gap was measured as its magnitude was varied. Observations made when true metallic contact had been made certain in the manner described showed the resistance to be quite constant under such conditions, varying only as points of contact between the films varied in their distance from the conducting clamps. Observations of the resistance of the gap were then made, usually at every quarter wave-length increase in the shortest distance between the films. Readings secured in this manner are given in Tables VII., VIII., IX., and X. The potential applied was 1.4 volts, supplied by one dry cell. Infinite resistance in these tables is taken to mean that the resistance was greater than 9,000,000 ohms.

Tables.

In the following tables a row labelled (*A*) contains the values of the magnitudes in wave-lengths of the gaps at which conduction ceased, while one labelled (*B*) indicates the corresponding values for the resumption of conduction.

Table I.

(*A*) 2½, 1, 10, 2½, 2¾, 13½, 3¾, 1½, 3½, 1½, 2½, 1½, 3, 2½, 3½, 3¾.

Table II.

(*A*) 1½, 3½, 1½, 2½, 1½, 3, 2½, 3½, 2 , 7, 3¾, 9½, 6, 3½, 8, 2 , 6½, 1½, 1½, 1½, 2½, 4¼, 2 , 2 .
(*B*) 1½, 4, 7½, 3½, 2, 1½, 1½, 1½, 1¼, 1 , 1¾, 2 , 1½, 1¾.

Table III.

(*A*) 1½, 2¾, ¾, ¾, 1, 1, 1½, 3½, 5¼, 3½, 2½.
(*B*) ⅝, ½, 1, 1¼, 2¾, 4¾, 3⅛, .

Table IV.

(*A*) 3, 2, 2 , 3 , 2 , 3 , 2, 2 , 1½, 2–.
(*B*) 2, 1, 1¼, 2½, 1¼, 1½, 1, 1½, 1 , 1¼.

Table V.

Volts.	Amperes.	Ohms.
.06	.00066	91
.07	.00070	100
.10	.00060	166
.155	.00086	174
.20	.00120	166
.175	.00105	157
.22	.00130	170
.23	.00135	170
.24	.00140	170
.25	.00170	150
1.238	.00820	150
1.345	.00840	160

TABLE VI.

In row (*C*) of this table are given the magnitudes in wave-lengths of the gaps across which the higher voltage discharges occurred.

(For Preliminary Potential Differences.)

(Volts)	3	3	4	4	3	4¾	3¾	3½	2¾	3¼	3	3	3¼	3½	3	3	3	4
(*A*)	1½	4½	2½	3	1½	2	2	1¼	2	2½	1½	4	2½	1½	2	2	2	3½
(*B*)		2	½	1½	1¼	1½	1	½	1½	1¼	1	2½	1½	1	1	1½	1½	1½

(For Higher Potential Differences.)

(Volts)	40	23	30	40	31	40	38	60	64	27	70	60	53	36	36	25	15	67
(*C*)		2½	2	3½	1¾	2	1¼	4½	2	1½	2¾	3	2½	1¼	1	1½	1½	5½

In Tables VII., VIII., IX., and X., row (*D*) gives the magnitude of the gap in wave-lengths, while row (*E*) gives the respective resistances in ohms.

TABLE VII.

(*D*)	0	¼	½	¾	1	1¼	1½	1¾	2	2¼	2½
(*E*)	8–	8	9	9⅓	9½	10	11	13	15	50	inf.

TABLE VIII.

(*D*)	0	¼	½	¾	1½
(*E*)	13.4	23.6	29.4	31.8	inf.

TABLE IX.

(*D*)	0	¼	½	¾	1	1¼	1½
(*E*)	19	45.7	65.5	200	40,000	3,000,000	inf.

TABLE X.

(*D*)	0	¼	½	¾	1	1¼	1½	1¾	2	2¼	2½	3½	4
(*E*)	16.4	19.6	21	23.1	25.2	28.8	31.7	34.7	37	37.5	45.8	4,600	9,999

* * * * * * * *

(Continued.)

(*D*)	4½	5	5½	6	6½	7	8¼	8½	9½
(*E*)	14,100	20,000	33,000	160,000	250,000	450,000	1,200,000	3,200,000	inf.

With certain films, conduction continued in some cases until the films had been separated more than 50 wave-lengths. The magnitude of the distance of separation of the electrodes for cessation of conduction varied greatly with the points on the electrodes nearest contact, but it was impossible to bring some films within three wave-lengths of each other without conduction. It was only after repeated trials with the making of the deposits and with particular care to keep the films at all times protected from dust particles that films were secured which could be brought very nearly together without conduction.

In order to obtain an indication of the nature of the medium providing conduction across the gaps, a test of Ohm's law was made for a constant gap of about 2¾ wave-lengths at which there was a considerable resistance. The electrodes were connected in series with a milliammeter, and various voltages applied, the potentials being determined by a voltmeter constantly shunted across the gap. The results are given in Table V.

For the same reason, the electrodes were left separated by a constant gap whose resistance was about 25.5 ohms, and 3 milligrams of radium contained in a lead case with a small slit were brought from a distant room to a position very near the electrodes. No change could be observed in the resistance of the gap.

It should be noted that the question of chief significance is not across how large an apparent gap conduction could be observed, but how nearly the electrodes could be made to approach without conduction. Since the films were observed to be continuous over the whole opposed surfaces of the lenses, and since considerable areas were separated by practically the same minimum distances, if any one spot could be found at which the electrodes could be brought within two wave-lengths of each other without conduction, and if it were certain that the remainder of the circuit were complete at the same time, this one observation would be sufficient to show that there could not be a general and uniform atmosphere of free electrons extending more than one wave-length above each metal surface, and conduction across apparently greater gaps at other places could be explained by a probable roughness of the surfaces.

Because of this consideration, observations were made of the magnitude of the gaps necessary for no conduction, without finding the values of the resistance during the intermediate steps. The films were first brought into contact and conduction assured. Then they were gradually separated and the point noted at which conduction ceased. Causing the electrodes to approach in such a manner that the point nearest contact should remain as nearly as possible the same throughout the observation, the films were next made slowly to approach each other, and the magnitude of the gap at which conduction was resumed was noted. Such observations were made at various places over the areas of the films. Readings secured in this manner are given in Tables I., II., and III. In each the potential difference applied was 1.4 volts, with the exception of the last ten readings in Table II., which were taken with 2.8 volts.

As a check, similar observations were made in a different manner. The electrodes, one dry cell, and the sensitive galvanometer were connected in series, and the positions for no conduction were taken as those positions at which no deflection of the galvanometer could be observed when the circuit was closed. It should be noted that before or after each reading conduction was secured by bringing the films into contact, thus making sure that the lack of conduction was not due to a break in any other portion of the circuit. Readings secured in this way are given in Table IV.

It was next decided to find just how large potential differences must be applied in order to break down the resistance of the very short gaps which proved insulators for small voltages. A rheostat of considerable resistance was connected directly in a D.C. circuit. Between one end of this and the sliding contact were shunted the electrodes, a resistance of 62,000 ohms, and the galvanometer, all in series. A voltmeter was left permanently shunted across the same two points. The films were first brought together and conduction established with very low voltages. They were then slowly separated and the positions at which conduction ceased were noted, after which they were brought together with the same voltage and the positions at which conduction was resumed were determined. When a spot had been found in this way where the electrodes could be made to approach very closely without conduction with low voltages, they were separated to a distance just greater than that at which conduction with low voltages was known to occur, and the magnitude of the gap kept constant. The applied voltage was then very slowly increased. It was found that as the potential was increased the electrostatic attraction between the electrodes became so great that they were drawn together, but by observing the rings the distance of separation at any instant could be discerned. By waxing a weight to the lower surface of the lower lens, and by slowly turning the thumbscrews in a direction tending to separate the electrodes as the potentials were increased, the magnitude of the gap could be kept quite constant. Since this magnitude could be continuously observed, the electrodes were sometimes separated by a distance greater than that at which it was desired to test the discharge potential, and then allowed to drift down to that distance, the extent of the gap across which conduction first occurred being noted in each case. Although conduction was understood to have taken place whenever the galvanometer began to be deflected, tiny clicking sounds could sometimes be distinguished when the gap was considerably greater than that across which general conduction occurred.

From the readings given in Tables I., II., III., IV., and VI., it is seen that with applied potentials of the order of a volt, it was possible to bring the electrodes so close together that their nearest points were separated by a gap of one half wave-length before conduction took place. This shows that at these points, and necessarily over a considerable area surrounding them, no medium conducting at such potential differences could have extended farther than one fourth wave-length beyond the metallic surface of each electrode.

It should be noted that when conduction was first established by bringing the electrodes into contact, after which they were slowly separated, conduction persisted in most cases across a much larger gap than that at which conduction was resumed, although great care was taken that the point nearest contact during the approach should be the same as that during the separation. Such a lag might be explained by the presence of long dust particles which would adhere to the two surfaces as they were being separated but which, after the circuit had been broken, would fall down so that the upper lens must descend much lower before reëstablishing contact. Or we might suppose that the particles were distended due to the electrostatic forces acting upon them. It would be difficult to conceive of such a pronounced effect with a uniformly distributed medium.

When the magnitude of a gap was left constant and the current measured for various potential differences, the ratio of the potential difference to the current was, as shown in Table V., as nearly constant as might be expected in the case of a metallic conductor, if one considers the possibility of vibrations of the electrodes and the accuracy with which the ammeter and voltmeter could be read.

Tables VII., VIII., IX., and X. were included as representative of the manner in which the low voltage conductance varied with the magnitude of the gap. If the relative variation be represented by curves, it will be seen (from those representing the data in VII. and VIII.) that the conductivity may vary in a random manner with the extent of the gap. Those for IX. and X., however, have a considerable regularity and the curve (Fig. 2) drawn from the data in X., in which the logarithm of the resistance is plotted against the magnitude of the gap, shows that there were three distinct phases in the variation of the conductivity in this particular case. If the conduction here is to be explained in terms of electron atmospheres, it would seem that we must grant them the privilege of existing in three distinct layers.

It would be much more natural to conclude that the conduction was due to dust particles of different dimensions.

It may be noted that in the case of reading no. (15), Table VI., the potential gradient for discharge if we consider the gap to be the distance between the reflecting surfaces of the films, was about 640,000 volts/cm., while if we consider the gap to be merely the increase over the largest which provided conduction at low potentials, the gradient was practically infinite. When compared with the 30,000 volts/cm. required for discharge across large air-gaps, this seems significant in its relation to the minimum discharge potential theory.

Because of the fact that the two electrodes could be brought within a distance of from one to one half wave-length from each other without conduction with applied potential differences as high as 36 volts, it seems that a uniform atmosphere of free electrons conducting for low voltages

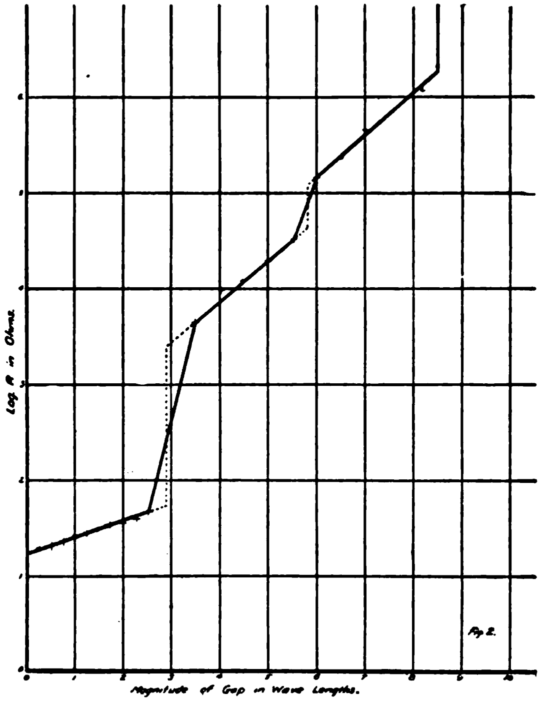

Fig. 2.

can not extend more than half that distance beyond the true metallic surface of a gold electrode.

Because of the fact that Ohm's law held for a considerable gap, because the proximity of radium produced no effect upon the conductance of the gap, because conduction persisted over a longer gap upon separation than that across which it was resumed when the electrodes were brought together, because electrodes could be brought nearer contact without conduction when particular care was taken to keep them entirely free from dust, because of the tiny clicks heard during the operations made in securing the data for Table VI. before general conduction was observed, and because of the peculiar forms of the curves showing the relations between the magnitudes of the gaps and their resistances, the writer feels confident that the conduction across the gaps as observed was due to small metal projections or to dust particles; rather than to a uniformly distributed medium.

The data showing the value of the voltages necessary for electrical discharges serving as insulators for small differences of potential, indicates that a minimum potential may be required to force an electrical discharge across small air gaps, or at least that the potential gradient required is much greater than that required across larger gaps.

The writer wishes to thank Professor W. F. G. Swann for the very kind advice and encouragement which he extended throughout the course of this work.

Department of Physics,
University of Minnesota,
June 12, 1922.

THE EFFECT OF CERTAIN DISSOLVED SUBSTANCES ON THE INFRA-RED ABSORPTION OF WATER.

BY J. R. COLLINS.

SYNOPSIS.

Infra-red absorption spectra of aqueous solutions of sixteen inorganic compounds from 0.8 to 2.3 μ, have been determined to see how the dissolved substances affect the absorption of the water. Care was taken to eliminate stray light by using two constant deviation glass spectroscopes in series. Readings were taken alternately with a cell containing a solution and with one containing water. Curves were thus obtained for the *alkali hydroxides, five chlorides (Al, Ca, Mg, Na, Sr), five nitrates (Ag, Al, Mg, NH_4, Zn) and three sulphates (Ag, Na, Zn).* (Figs. 3–16). All solutes decreased the absorption in the water band at 1.44 μ and probably also in the band at 2 μ, whereas all excepting $Al_2(SO_4)_3$, $ZnSO_4$ and the hydroxides increased the absorption in the bands at 0.97 and 1.2 μ. These results do not agree with the solvate theory which ascribes the effect to the formation of hydrates, since some non-hydrating compounds decreased the absorption at 1.44 μ.

Absorption of water, from 0.8 to 2.3 μ, was measured by using cells of different known thicknesses. *The wave-lengths of maximum absorption* were found to be 0.97, 1.20, 1.44, and 2.00 μ, and the corresponding *coefficients* came out 0.448, 1.220, 29.4, and 103, respectively. Such difference as there is between these results and those previously obtained may be due to elimination of stray light. The fact that in the absorption spectrum of water vapor the bands at 1.44 and 2 μ are stronger and the other two bands weaker than for liquid water suggests that the former two bands are associated with a different kind of molecule than the latter two bands. If so, the effect of a dissolved substance on absorption may be due to a change in the relative number of these kinds of molecules produced by the presence of the substance.

INTRODUCTION.

IN their study of infra-red absorption spectra of aqueous solutions, Guy, Schaeffer, and Jones[1] found that, in some cases, the solutions were more transparent than the water present would be if there were no dissolved substance in it. Schaeffer, Paulus, and Jones[2] studied this effect of dissolved substances on the absorption of water further and found that the change in the absorption of the water was generally accompanied by a slight shift in the position of the absorption band toward the longer wave-lengths. Grantham[3] found that the alkaline hydroxides dissolved in water caused a decrease in the absorption of water at one absorption band, the effect due to these substances being greater than that due to the inorganic salts studied by the previous investigators. No conclusion can be drawn as to a shift in the position of the absorption band caused by the alkaline hydroxides, since the hydroxides have an absorption band which overlaps that of water, thus making it impossible to distinguish the exact form of either absorption band. Further evidence of a shift in the position of an absorption band of water by dissolved substances was obtained by Ångstrom,[1] who measured the reflection of infra-red radiation from the surfaces of solutions. A shift in the positions of maximum and minimum reflection is interpreted as a shift in the position of the absorption band. No information was obtained as to changes in the intensity of absorption of the water.

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[1] Phys. Zeitschr., 14, p. 278 (1913).

[2] Phys. Zeitschr., 15, p. 447 (1914).

[3] PHYS. REV., 18, p. 339 (1921).

The most intense absorption bands of water occur at about 3 μ and 6 μ. Nearer the visible spectrum there are four much less intense bands which differ greatly among themselves in intensity. These bands were located by earlier observers at about 1.0 μ, 1.2 μ, 1.5 μ and 2.0 μ, this order being also one of increasing intensity. Jones and his co-workers studied the effect of dissolved substances on the absorption of water in the spectral region including the first two of these bands. Grantham's results on the effect of the alkaline hydroxides are confined to the absorption band at 1.5 μ. Ångstrom worked in the near infra-red, but obtained results only for the intense absorption band at 3 μ.

The absorption bands of water at 3 μ and 6 μ are so intense that extremely thin layers are necessary for their study, so that a quantitative comparison of the absorption of solutions and water would be very difficult. The other four absorption bands mentioned above are such that measurable thicknesses can be used and an accurate comparison made. It was the purpose of this investigation to study the effect of various dissolved substances on the absorption of water throughout the spectral region containing these four absorption bands.

Apparatus and Experimental Procedure.

It was necessary to obtain a spectrometer system free from appreciable stray radiation. Since no single spectrometer was at hand in which the stray radiation was negligible, two spectrometers were used, one serving as a monochromatic illuminator for the slit of the second. As measurements were to be made to 2.3 μ only, spectrometers with glass lenses and prisms were used. The spectrometers were of the constant deviation type and arranged as illustrated in Fig. 1.

The source of radiation, S', is a series street lighting lamp with a single spiral filament set vertically. It was run on storage batteries to insure constant current. L_1 is a lens so placed as to render the light from S' parallel. Diaphragms D_1 and D_2 were placed in the beam to limit this beam, so that its cross-section was smaller than that of the cells under investigation. These cells were mounted on a slider P'. This slider could be moved by the observer by means of cords, so that either cell or an opaque screen was placed in the beam. L_2 is a lens which formed an image of the lamp filament on the slit S_1 of the first spectrometer. L_3, P_1, and L_4 are the collimator lens, prism, and telescope lens respectively, of this spectrometer, the spectrum being focused in the plane of the slit S_2 of the second spectrometer, of which L_5, P_2, and L_6 are the collimator lens, prism and telescope lens respectively. The spectrum is focused in the plane of the slit S_3, behind which a Coblentz thermopile is mounted. The thermopile is connected to a Coblentz ironclad galvanometer which was read by means of a telescope and scale.

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[1] Phys. Rev., 3, p. 47 (1914).

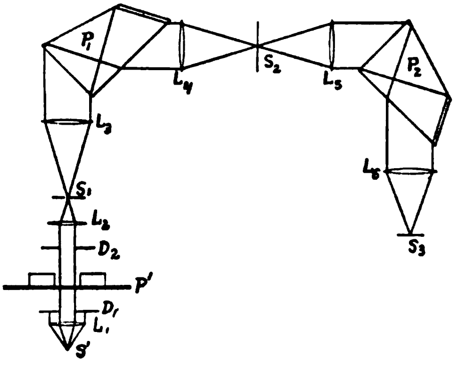

Fig. 1.

The second spectrometer was used to indicate the wave-length of the radiation incident on the thermopile. The scale on the drum was divided uniformly, the smallest divisions corresponding to a range of about 0.3 $\mu\mu$ in the visible spectrum. This spectrometer was calibrated by observing the drum readings corresponding to the positions of the emission lines of sodium, lithium, potassium and mercury. The lines of the first three metals were obtained by volatilizing their salts in the open arc, and a quartz mercury arc was used for the mercury lines. A considerable number of lines were easy to locate and the location of the lines in the visible region could be checked visually. The wave-lengths of these lines were obtained from Paschen's data.[1]

The cells to contain the liquid under test consisted of two pieces of plane parallel quartz or pyrex glass between which, for the thicker cells, was placed a glass tube with plane parallel ends filled with the liquid. For the thinner cells washers of thin glass or celluloid were used. Since the two spectrometers were used in series it was necessary that the cells have plane parallel ends and that the liquid be of uniform thickness over the entire cell. Otherwise a change in the direction of the beam of radiation resulted in a change in the amount of radiation reaching the thermopile even with no absorption. Thus two pieces of transparent quartz, one plane parallel and the other slightly wedge shaped, appeared to have different transmissions when placed alternately in the beam of radiation. This effect was not noticeable if the variations in thickness were not more than 0.001 cm. in a plate of 3 cm. diameter.

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[1] Ann. d. Physik., 27, p. 537 (1908).

The coefficient of absorption of water was determined throughout the spectral region 0.8 μ to 2.3 μ by finding the absorption of known thicknesses. In order to avoid the error due to reflection at the surfaces of the cells, two cells of different thicknesses were mounted on the slider P' (Fig. 1) and the deflections of the galvanometer observed when the cells were placed in turn in the beam entering the spectrometer system. The ratio of these deflections gives the fractional transmission of a layer of water equal in thickness to the difference of thicknesses of the two cells.

The fractional transmission of the solutions was obtained by mounting on the slider P' two cells of approximately the same thickness, one containing the solution and the other containing pure water. The galvanometer deflections were observed when these cells were placed in turn in the beam of radiation. The ratio of their transmissions were thus obtained. The fractional transmission of the water could be computed from the known coefficients of absorption and then the fractional transmission of the solution calculated from that of water and their ratio. There are two advantages of comparing the transmission of the solution to that of water instead of determining the fractional transmission of the solution by using two cells of solution. First, it is the object of the experiments to compare the transmission of the solution with that of water and this method does that with one set of observations instead of two. Second, a small error in the wave-length setting of the spectrometer on the side of an absorption band will cause a large change in the fractional transmission observed if the fractional transmission of the solution is determined directly; the ratio of the transmission of the solution to that of water does not change so rapidly as we proceed along the spectrum as does the fractional transmission, hence a small error in wave-length setting does not affect the results so much.

Since the four absorption bands of water have different intensities, the cells to contain the liquid were of different thicknesses for each of the four parts of the spectral region studied. These thicknesses were: about 2 cm. for the range 0.8 μ to 1.1 μ; about 1 cm. for the range 1.1 μ to 1.3 μ; about 0.04 cm. for the range 1.3 μ to 1.7 μ; about 0.025 cm. for the range 1.7 μ to 2.3 μ.

EXPERIMENTAL RESULTS.

I. *The Absorption Spectrum of Water from 0.8 μ to 2.3 μ.*

The fractional transmission of water for known thicknesses was carefully determined throughout the spectral range studied. The agreement of the values of absorption coefficients calculated from the observed transmission of widely different thicknesses of water indicate that the apparatus was free from appreciable stray radiation. A comparison with the values obtained by Aschkinass[1] and also those calculated from the data of Jones and his co-workers[2] can be made only at the positions of maximum absorption since the wave-length calibration of the prism used by Aschkinass was apparently not correct.[3] Table I. gives the values of the absorption coefficients at these positions.

TABLE I.

Position of Maximum Absorption.	Coefficients of Absorption.		
	Aschkinass.	Jones et al.	Collins.
.97 μ	.416	.446	.448
1.20 μ	1.221	1.297	1.220
1.44 μ	38.4	——	29.4
2.00 μ	123.2	——	103

The agreement at the first two absorption bands at .97 μ and 1.20 μ is remarkably good. At the other two bands, however, the agreement is not good. The thicknesses used by Aschkinass were much smaller than those used in the present investigation and could not be measured so accurately by the method used by him. This may be a possible explanation of the differences shown in Table I.

As may be seen from Table II., the wave-lengths of maximum absorption as determined in the present investigation do not agree with those obtained by some earlier observers. The care taken in eliminating stray radiation in the present investigation may account for some of the differences in the positions of the absorption bands as compared with the results of others.

II. *The Absorption Spectra of Aqueous Solutions.*

In order to compare the absorption spectra of the solutions with that of water the amount of water in each solution was computed from a knowledge of the concentration and density of the solution. Then two curves were plotted on the same axes: (1) the per cent. transmission of

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[1] Ann. d. Physik, 55, p. 401 (1895).

[2] Loc. cit.

[3] See Coblentz, Carnegie Inst. of Wash. Pub. 65 (1906).

TABLE II.

Observer.	Date.	Kind of Prism.	Position of Maximum Absorption.			
Paschen.......	1894	Fluorspar	——	——	1.51 μ	2.05 μ
Aschkinass....	1895	Flint Glass	1.00 μ	1.24 μ	1.50	1.96
Donath.......	1896	Flint Glass	——	——	1.45	1.96
Coblentz.....	1910	Fluorite	——	——	1.48	1.95
Grantham.....	1921	Rocksalt	——	——	1.48	1.98
Collins........	1921	Flint Glass	.97	1.20	1.44	2.00

the solution as a function of the wave-length and (2) the per cent. transmission of a layer of water equivalent to that present in the solution. Four curves are plotted for each substance as different thicknesses had to be used for different parts of the spectral region studied. The thicknesses of layers used were in all cases those indicated in Fig. 3. If the dissolved substance has an effect on the absorption of the water or has an absorption of its own the two curves would not coincide. If the transmission curve for the solution lies above that for water, the dissolved substance has had an effect on the absorption of the water. If, however, the curve for the solution lies below that for the water, there are two possible explanations and in general it is impossible to separate them. It seems unlikely that the absorption bands for the dissolved substance would lie exactly at the same position and have the same shape as the water absorption band, so that the transmission curves for the solutions should be distorted from those of water if the dissolved substances have absorption bands in the region studied. An example of this is shown in Fig. 2.

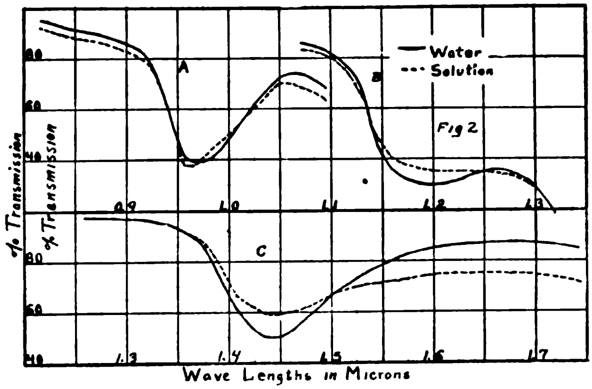


Fig. 2.

5N solution of NaOH. 200 grams per liter. Density 1.186 gr./c.c.

Solutions of NaOH, KOH and LiOH were studied and curves for NaOH only are shown as they are typical of the results for all three substances. Grantham has already studied solutions of these substances in the region of the absorption at 1.44 μ and showed that all of them rendered the water less absorbing in that band in spite of an absorption band of the substances themselves which overlaps that of water. Curves *A* and *B* of Fig. 2 show the effect of NaOH on water in the bands at .97 μ and 1.20 μ. At 1.20 μ there is a decided increase in the transmission but at the other band there is a decrease in transmission on one side of the band. From the distorted shape of the solution curve it was suspected that the hydroxides had absorption bands near .96 μ, 1.1 μ and 1.27 μ. Concentrated solutions were made of KOH in absolute methyl alcohol and absolute ethyl alcohol and the transmission curves determined. Absorption bands were found at the wave-lengths .95 μ and 1.1 μ and 1.26 μ. It seems safe to say then that these three alkaline hydroxides make water more transparent in all three of the absorption bands shown in Fig. 2.

Figures 3 to 15 show the results obtained for several salts, all except the last three being hydrating substances. $Al_2(SO_4)_3$, $ZnSO_4$ and the alkaline hydroxides decrease the absorption of water in all four absorption bands studied. All other substances studied decreased the absorp-

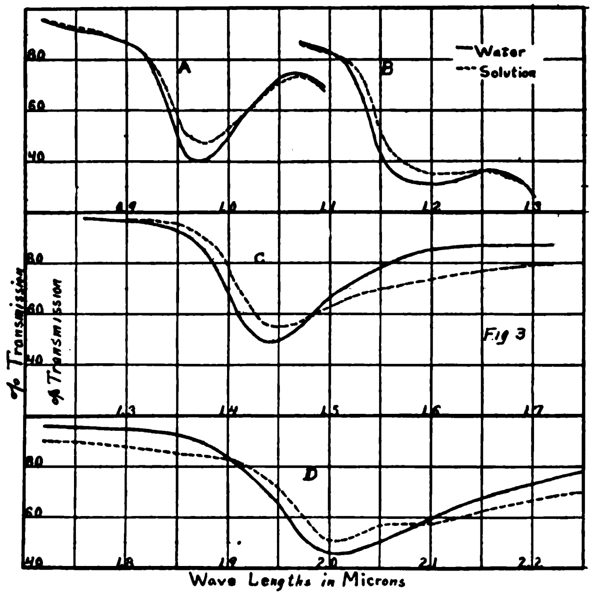
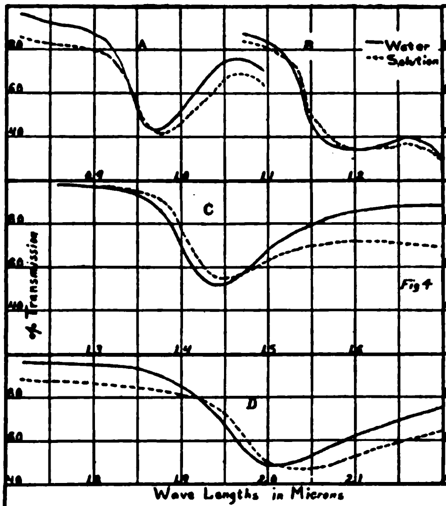
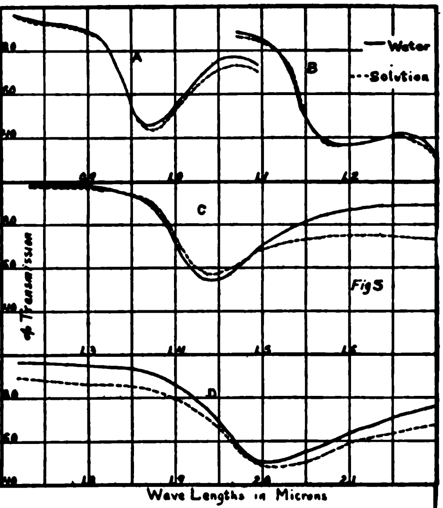


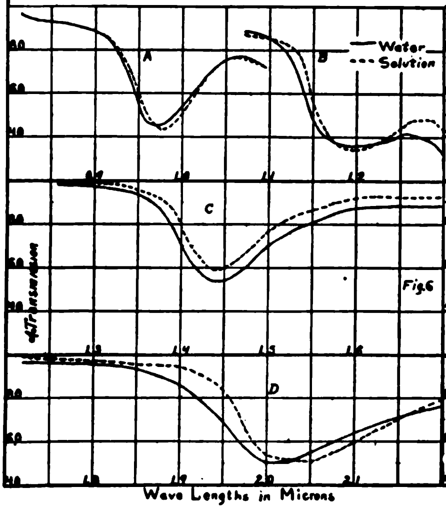
Fig. 3.

$Al_2(SO_4)_3$. 259.3 gr./liter. Density, 1.2200 gr./c.c.
Curve *A*, 2.090 cm. layer of solution. Curve *B*, .997 cm. layer of solution.
Curve *C*, .025 cm. layer of solution. Curve *D*, .0079 cm. layer of solution.

tion in the absorption band at 1.44 μ, increased the absorption in the absorption bands at .97 μ and 1.20 μ. The absorption band at 2.00 μ is not affected in the same way by all substances but in most cases where







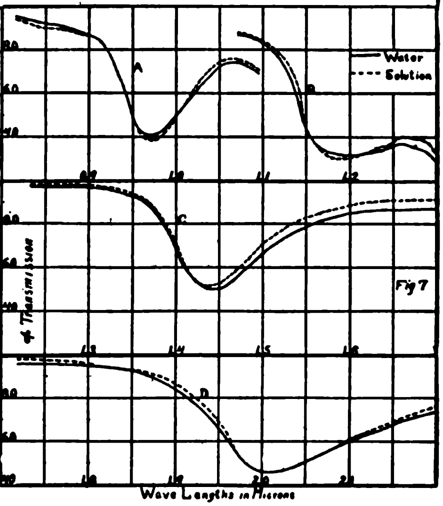


Fig. 4.

$AlCl_3$. 326.0 gr./liter. Density, 1.2133 gr./c.c.

Fig. 5.

$Al(NO_3)_3$. 430 gr./liter. Density, 1.2517 gr./c.c.

Fig. 6.

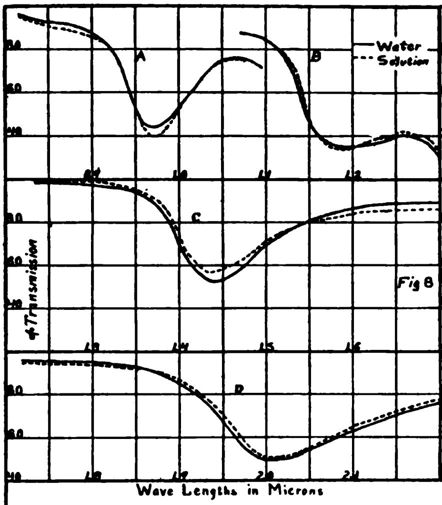
$CaCl_2$. 557.7 gr./liter. Density, 1.3950 gr./c.c.

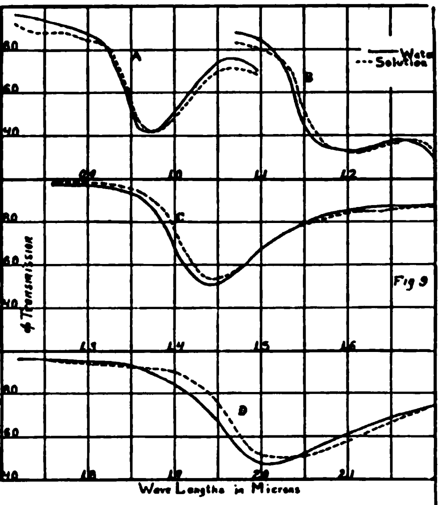
Fig. 7.

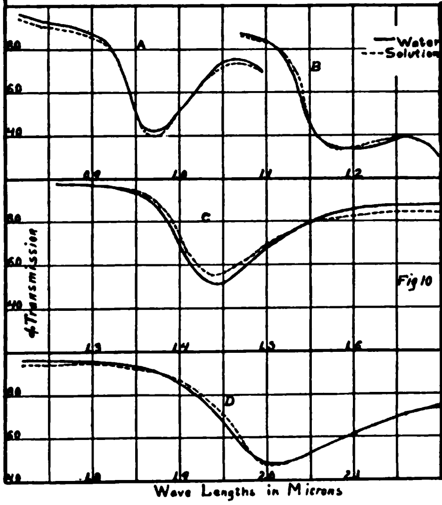
$SrCl_2$. 296.0 grams/liter. Density 1.2445 gr./c.c.

the absorption is increased the irregularity of the curve for the solution indicates that the dissolved substance had absorption bands in this region.

No definite conclusions can be drawn as to shifts in the positions of







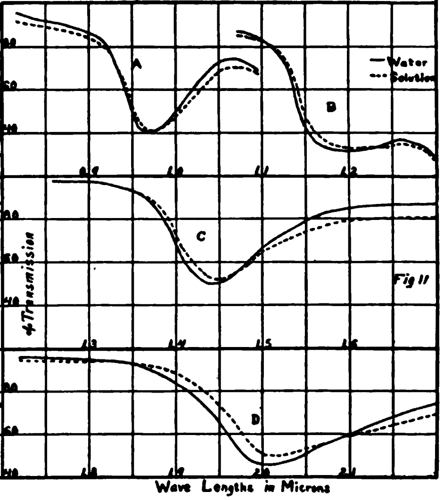


Fig. 8.

$Mg(NO_3)_2$. 424.5 gr./liter. Density, 1.2873 gr./c.c.

Fig. 9.

$MgCl_2$. 319.0 gr./liter. Density, 1.2360 gr./c.c.

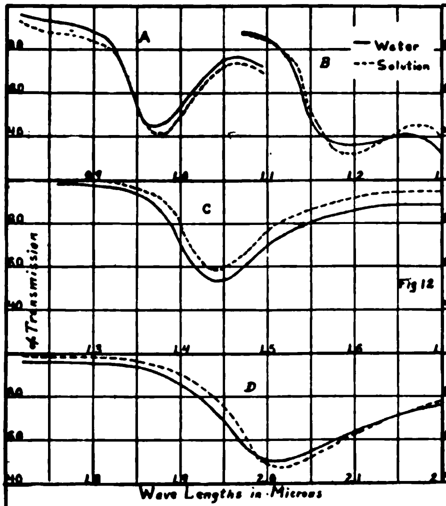
Fig. 10.

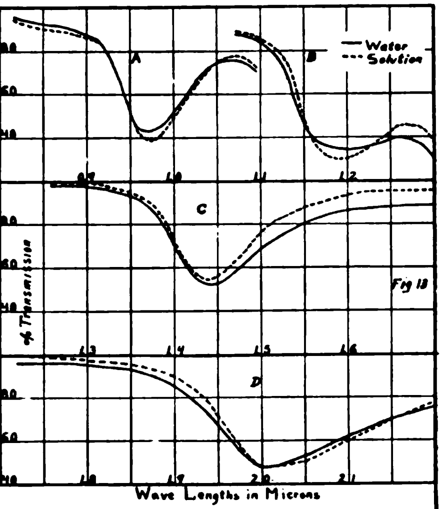
$Zn(NO_3)_2$. 414.5 gr./liter. Density, 1.3200 gr./c.c.

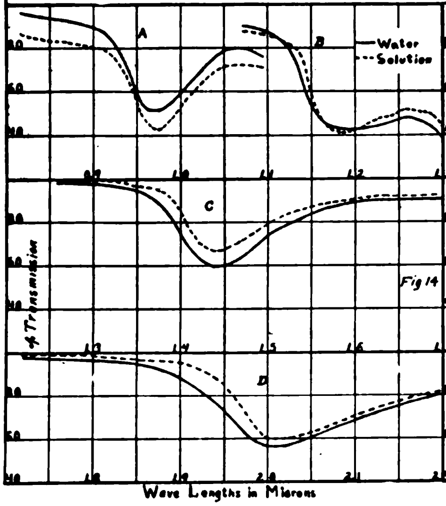
Fig. 11.

$ZnSO_4$. 513.0 gr./liter. Density, 1.466 gr./c.c.

the water absorption bands due to the dissolved substances. In most cases where there is an apparent shift in the position of maximum absorption it is difficult to say that it is a true shift, as the presence of







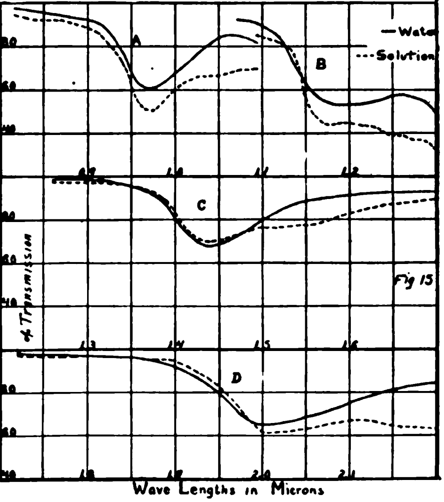


Fig. 12.

$Na_2S_2O_3$. 524.9 gr./liter. Density, 1.361 gr./liter.

Fig. 13.

NaCl. 319.8 gr./liter. Density, 1.2020 gr./c.c.

Fig. 14.

$AgNO_3$. 1413.0 gr./liter. Density, 2.1180 gr./c.c.

Fig. 15.

NH_4NO_3. 743.0 gr./liter. Density, 1.2700 gr./c.c.

an absorption band of the dissolved substance near that of the water might cause such a change in the shape of the curve.

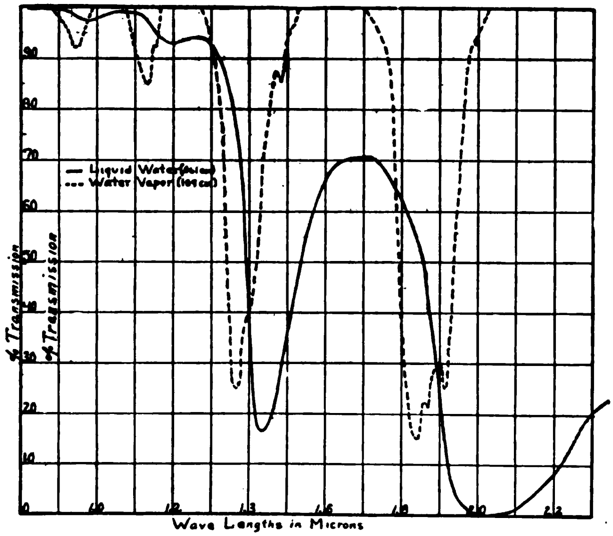


Fig. 16.

DISCUSSION.

Schaeffer, Paulus, and Jones explained their results on the basis of the solvate theory. The dissolved substances which form loose combinations with some of the water in which they are dissolved render this part of the water less absorbing. Non-hydrating substances should have no effect on the absorption of the water. Their explanation did not fit all the data which they published and does not agree with all the results shown here. $Al_2(SO_4)_3$, $ZnSO_4$, and the alkaline hydroxides make the water less absorbing at all the absorption bands, but all the remaining hydrating salts studied cause a greater absorption at some of the absorption bands. Also the three non-hydrating salts, NaCl, NH_4NO_3, and $AgNO_3$ all caused a decrease in absorption by water at one absorption band.

Livens[1] has deduced an explanation of an effect of a dissolved substance on the absorption of the solvent on the basis of the Lorentz electron theory. If the solute has absorption bands at wave-lengths much longer than that of the solvent, the solvent should absorb less than it would if the solute were absent and the position of maximum absorption should be shifted toward the shorter wave-lengths. If the solute has absorption bands at wave-lengths shorter than that of the solvent, the solvent should be more absorbing in the presence of the solute and the position of maximum absorption should be shifted toward the longer wave-lengths. This explanation would seem to lead to the conclusion that all the absorption bands of water here studied should be affected alike, as they lie close together and thus have the same relation to the absorption bands of the dissolved substance.

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[1] Phys. Zeitschr., 14, p. 660 (1913).

Neither of these explanations fits the experimentally determined facts completely. With the exceptions of $Al_2(SO_4)_3$, $ZnSO_4$ and the alkaline hydroxides, the solutes used caused an increase in the absorption of the water at the absorption bands located at .97 μ and 1.20 μ, and a decrease in the absorption of the water at the band located at 1.44 μ. From an examination of the curves it seems likely that the dissolved substances decrease the absorption of the water in the band at 2.00 μ, although in many cases this effect is apparently masked by the presence of absorption bands of the dissolved substance.

With the above exceptions then it may be said that the effect of dissolved substances is to increase the absorption of the water at two absorption bands (.97 μ and 1.20 μ) and to decrease the absorption of the water at the other two bands (1.44 μ and 2.00 μ). A parallel to this is found by comparing the absorption of water vapor and liquid water for layers having equal number of molecules. Fig. 16 shows the absorption spectra of equivalent thicknesses of water vapor and liquid water. The water-vapor curve is taken from the results of Hettner.[1] There is an absorption band in the vapor curve for each band in the liquid curve, but displaced toward the shorter wave-lengths. The absorption bands of water at .97 μ and 1.20 μ are less intense than the corresponding bands for the vapor, while the bands at 1.44 μ and 2.00 μ are more intense than the corresponding vapor bands. This fact suggests that there may be some connection between the effect of dissolved substances on the absorption of water and the effect of changing from vapor to liquid.

The fact that all the absorption bands of liquid water are present when the water is converted into vapor indicate that these absorption bands are due to the molecules and not to aggregations of molecules. Hence it seems that the only way in which the absorption could be changed to a great extent would be by a change in the number of absorbing molecules present. If there are different kinds of water molecules there is a possibility of their relative number being changed by the presence of a dissolved substance, by polymerization of the water, by change of temperature, etc. According to Langmuir's[2] model of the water molecule there may be four kinds of water molecules as the hydrogen nuclei may be arranged in four different relative positions about the oxygen nucleus. These different molecules would probably have different modes of vibration which would give rise to absorption bands of different frequencies. The relative intensities of these absorption bands would depend in part on the relative number of each kind of molecule present in the water. Some such explanation together with the fact that some dissolved substances form loose combinations with the water in which they are dissolved may be able to fit the experimental results when more data are available. At present no simple explanation fits all the known results.

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[1] Ann. d. Physik., 55, p. 476 (1919).

[2] Jour. Amer. Chem. Soc., 41, p. 893 (1919).

The writer wishes to thank Professor R. C. Gibbs, under whose direction the investigation was carried out, for his encouragement and helpful advice during its progress.

CORNELL UNIVERSITY.

THE EXISTENCE OF HIGH MOBILITY IONS.[1]

By Oswald Blackwood.

Synopsis.

Existence of Positive Ions of Abnormally High Mobilities in Air.—Contrary to the conclusions of other observers, Nolan has reported what he believes to be indications of the presence in ionized moist air of ions of eight different mobilities ranging from one to seven times the normal value. *A repetition of Nolan's experiment,* however, with duplicate apparatus, has led to an explanation of his anomalous results. In his experiment, ions generated in a small shielded space next the lower plate of a long condenser, are carried by an air current into the electric field where the mobility is determined by a blast method. At first curves similar to Nolan's were obtained, but the irregularities interpreted as due to different groups of ions were removed when precautions were taken to insure a uniform blast of air. Then it was discovered by the author that in spite of a lead shield between the emanation tubes emitting the ionizing rays and the measuring chamber, there was, contrary to Nolan's assumption, a volume ionization in that chamber, due probably to secondary x-rays from the lead, which accounted for his results. When these secondary rays were eliminated by substituting polonium as the source of ionization the mobility came out normal.

Introduction.

The existence of small ions of very high mobility is indicated in several papers by Nolan,[2, 3] who finds a value *seven times* greater than normal. Furthermore, he detects in the ionization from radioactive bodies not *one* but *eight* widely separated sizes of ions. In so far as the writer knows, these results are at variance with the investigations of all other workers[4] who agree in assigning to the negative ion in dry and moist air mobilities 1.8 and 1.5 cm./sec. respectively. In particular, the normal value has been reported recently by Erikson[5] using a method closely resembling Nolan's.

The author has repeated the experimental work in detail, and in addition finds that the curves are capable of another interpretation and that, when certain precautions neglected by Nolan are taken, the method indicates the existence of but one size of ion of normal mobility.

Method.

The apparatus is fully described in Nolan's paper.[2] It consists of a shallow box 10 cms. in depth fitted with two condenser plates. The upper (electrometer) plate is 35 cms. long and is surrounded by an earthed guard ring. The lower plate may be given any desired potential. Ionization is produced in the small trough Z below a lead shield (See Fig. 3, Z) the source being several tubes of radium emanation lying on the floor of the trough. A current of air traverses the apparatus carrying ions from Z into the condenser. When the electric field is zero these ions are carried forward horizontally. As the field is increased step by step the stream is curved upward more and more until, at a critical voltage, it is forced into contact with the upper plate and the electrometer current jumps from zero to its maximum value. In practice owing to recombination, diffusion, turbulence of the air stream, as well as other factors, the ideal curve should not be realized.

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[1] An abstract of this paper was read by title at the December meeting of the American Physical Society.

[2] Proc. Royal Irish Academy, XXXV. (A), p. 38 (1920).

[3] Ibid., XXXIII. (A), p. 9 (1916). Proc. Royal Society, XCIV. (A), p. 112 (1918).

[4] Proc. Camb. Phil. Soc., IX., p. 401. Phil. Trans., A, 195, p. 193. Annale de Chemie et de Physique, XXVIII., 289. Proc. Nat. Acad., II. (1916), 345.

[5] Phys. Rev., XVIII., p. 100 (1921).

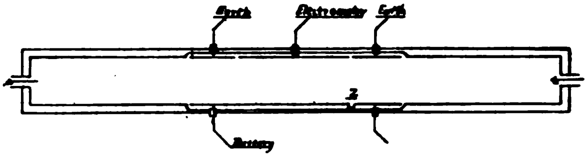

Fig. 1.

The mobility of the ions can be calculated from $u = vb^2/LV$ where V is the critical voltage at which ions begin to reach the plate, u is the ionic mobility, v the velocity of the air stream, b the vertical distance between the plates and L the plate length.[1]

Discussion of Results.

One of Nolan's typical current voltage curves for air saturated with water vapor is shown in Fig. 2. It will be noted that the curve does not cross the X axis at 14 volts as it should (1) if ions of normal mobility were present, and (2) if all the ions were produced at Z. Nolan interprets the fact that small voltages are sufficient to drive ions to the plate on the hypothesis of high mobilities. Furthermore, he explains the *eight* "nicks" or "steps" ($a \cdots f$, Fig. 2) as indicating the presence of eight different sizes of ions.

The writer has duplicated Nolan's apparatus in detail and has repeated his measurements using several different air velocities. The curves re-

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[1] At the critical voltage V the ions are displaced through the vertical distance b cm. between the plates while the air stream carries them through a horizontal distance L. The electric field (potential gradient) being V/b and the vertical speed Vu/b, the time to move through the condenser is

$$t = \frac{b}{Vu/b}.$$

Also, $t = L/v$. Therefore, $u = b^2v/LV$.

semble those of Nolan in that they pass through the origin, showing that small fields are sufficient to drive ions to the plate. They also have "nicks" or "steps" but these are not repeatable and are probably due to lack of constancy in the motion of the gasometers used to force air through the apparatus. After these gasometers were replaced by a constant-speed rotary pump the curves showed no irregularities. They show no evidence, therefore, of the existence of separate, distinct groups or sizes of ions.

The first inkling of an explanation of the form of the curve not involving the assumption of high mobilities came when the air stream in the ion box was reversed in direction. If all the ions were really produced in the shielded space *Z*, as Nolan assumed, this procedure should reduce the galvanometer current to zero, since the reversed air stream carries the ions *away* from the condenser. In fact, however, the current decreased only one third. Most of the ions, therefore, are produced in the main volume of the condenser.

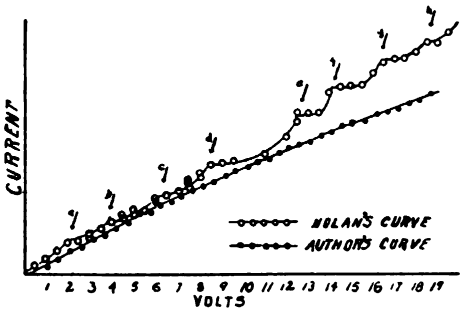

Fig. 2.

The distribution in still air of this general ionization has been studied as follows. A wire screen of 1 cm. mesh was placed horizontally between the two condenser plates. (See Fig. 3, *X*.) It was charged to the same potential as the lower plate so that no ions produced below it should be driven to the electrometer. The potential of the screen was given a sufficiently high value to drive all ions above it to the electrometer plate. The current was found to be directly proportional to the distance between the screen and plate. This indicated a uniform vertical distribution of the ionic density. Therefore, the ionization near the electrometer plate is as great as that in the lower part of the condenser. This being the

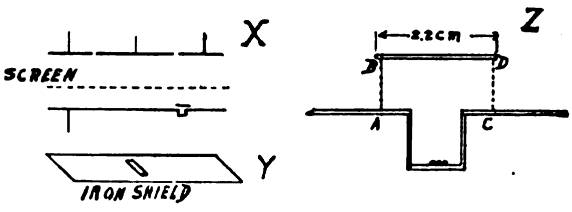

Fig. 3.

case, an explanation of the experimental curve is simple. Ions are driven to the upper plate by small fields not because the ions have ***high mobilities, as Nolan assumed,*** but because they are generated in ***immediate proximity*** to it.

SOURCE OF GENERAL IONIZATION.

With the purpose of discovering the source of this general ionization, its horizontal distribution in still air was investigated. The wire screen described above was replaced by a grounded sheet of iron which was fitted with an aperture four cm. wide. (See Fig. 3, Y.) This sheet of metal shielded the electrometer plate from all ions which were not generated immediately below the slit. Keeping the electric field constant, the sheet was shifted horizontally so as to successively uncover all portions of the upper plate. The electrometer currents for the various positions show that more than one third of all the ions are produced at distances from the ion trough Z greater than 10 cm.

In order to investigate the absorption of the rays causing the general ionization, the window CD (Fig. 3, Z) was blocked with a lead plate while AB was covered with a paper screen found to be equivalent to .001 cm. thickness of aluminium foil. This shield decreased the ionization about 50 per cent. Replacing the paper by a sheet of lead 1 mm. thick reduced it to zero. Since the window CD is shielded from direct radiation, and since the paper was adequate to prevent diffusion of ions into the main chamber, by elimination it seems probable that the general ionization was due to secondary Roentgen radiation from the lead walls of the trough at Z. While this radiation is doubtless relatively feeble, the volume of air penetrated by it is at least one hundred times that of the volume at Z which is subject to direct radiation.

An attempt was next made to eliminate secondary radiation and realize experimentally the intense, localized ionization which Nolan assumed to exist in his apparatus. The ionizing agent used was polonium which emits only alpha rays. The specimen was equivalent in ionizing power to about 1/40 mg. of radium bromide. With an air velocity of 4.1 cm./sec., several current-voltage curves were determined of which Fig. 4, A, is typical. This curve has only one break in slope corresponding to a critical voltage 7.5 and a mobility 2.15 cms./sec. It will be noticed that a considerable number of ions are driven to the plate at voltages less than 7.5. This was attributed to turbulence of the air stream and to secondary radiation. To decrease the former the height of the ion box was reduced fifty per cent., thus increasing the ratio of length to cross section. To lessen secondary radiation the shield over Z was lowered 5 millimeters thus decreasing the size of the openings through which the radiation might pass. Using the modified ion box only two curves were determined. (See Fig. 4, *B*.) The intercepts are much more sharply defined than in the case of the preceding curve. The computed mobilities, 1.96 and 2.13 cm./sec. are respectively within 30 and 42 per cent. of the accepted value for moist air. The agreement is not close, but it is sufficient to show that the method indicates the existence of only *one size* of ion of approximately normal mobility.

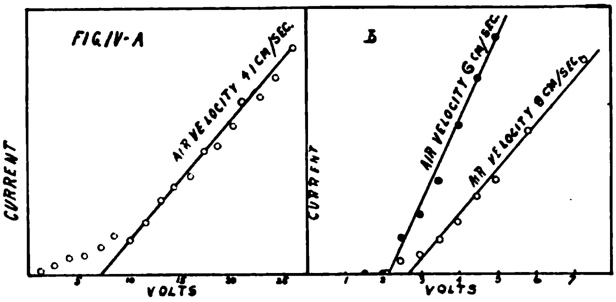

Fig. 4.

Summary.

1. Nolan has presented evidence indicating the existence of several sizes of high-mobility ions.

2. The writer, after duplicating the apparatus, finds no evidence for the existence of several groups.

3. General ionization, proved to exist in the tube, is adequate to explain the experimental curves. It is not necessary, therefore, to assume the existence of high mobility ions.

4. After eliminating general ionization, the method gives approximately the mobility value found by other workers.

Note Added October 10, 1922.

Further evidence as to the existence of the ions of high mobility has been reported by Nolan and Harris.[1] After adopting a more accurate alternating-field method, *they find no trace of the mobile ions*. The writer believes that this confirms his own results, but Nolan and Harris explain the failure to detect the ions on the assumption that in the new apparatus the ions recombine before reaching the electrometer plate. They write as follows:

"We think that the explanation lies in the one radical difference between the two methods. In the air-current method the ions of one sign are almost immediately separated from those of opposite sign and for practically all their path in the measuring vessel are moving through air free from other ions. In the alternating-field method the ions are in contact with one another for some time in the space above the perforated plate. The time that an ion spends in this space will depend upon the value of the field there, the distance from the place where it is formed to the perforated plate, and its mobility. . . .

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[1] Proc. Royal Irish Acad., Sect. A, XXXVI., p. 31, 1922.

"It seems to us reasonable to suggest that the alternating-field method fails to reveal the faster ions because they have disappeared by recombination. The older method does reveal them because the chances of recombination have been reduced to a minimum."

This explanation will be shown to be quite inadequate since the ions in the older method are by no means "immediately" removed from those of opposite sign. Indeed, the time available for recombination is actually much greater in the older apparatus. In this method the ions are produced in the space immediately below a lead plate 2.2 cms. wide (Fig. 1, *Z*), and are not subject to the electric field and, consequently, are not separated from those of opposite sign until they have moved forward an average distance of at least 1.1 cms. The air velocity being 6 cm./sec., the time available for recombination is at least 1/5 second. In the newer apparatus the ions after being produced in a box 4 cms. high are driven downward toward a perforated plate through which they pass into the condenser proper. Until they reach this plate they are in contact with ions of opposite sign and are subject to recombination. The mean distance to the plate is thus 2 cms., the field strength was 4 volt/cm. and the time available for recombination for the three fastest ions (mobilities 12, 7, and 4 cm./sec.) would be respectively 1/24, 1/14, and 1/8 seconds. Thus the times available for recombination were respectively 1.6, 3, and 5 times greater in the older apparatus than in the new.

After failing to detect the ions in moist air, Nolan and Harris next introduced a new condition by drying and, using the new apparatus, found an abundance of faster ions. These results, however, must be regarded with caution since they are quite opposite to those of Loeb,[1] who also used an alternating-field method. He dried the air so thoroughly that free electrons were detectable for several days, but found no trace of abnormally mobile ions.

THE UNIVERSITY OF PITTSBURGH,
DEPARTMENT OF PHYSICS,
PITTSBURGH, PA.

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[1] PHYS. REV., XVIII., p. 89, 1921; XVIII., p. 633, 1916. Nat. Acad. Sci. Proc. (6), p. 435, 1920.

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THE

PHYSICAL REVIEW.

A PHOTOGRAPHIC STUDY OF SOUND PULSES BETWEEN CURVED WALLS AND SOUND AMPLIFICATION BY HORNS.

BY ARTHUR L. FOLEY.

SYNOPSIS.

Photographic Study of Sound Pulses Passing between Walls Corresponding to Sections along a Straight Tube, a Crooked Tube, a Megaphone and a Conical Horn Receiver.—Using the photographic method previously developed by the author, four pairs of brass plates, each of the proper section, were arranged radially about the axis of the sound-producing spark so as to provide the four passages to be studied. As the sound pulse progressed through these passages, instantaneous photographs registered its position at various stages. Six of these are reproduced. They clearly show that whenever a pulse moves at an angle to a wall there is reflection in exact accord with Huygen's construction. Sound pulses, therefore, do not glide around bends in tubes without appreciable reflection. In the case of a pulse emerging from the open end of a tube or horn, the per cent. of the energy reflected is small, while much of the energy of a pulse entering the large end of a conical horn is reflected back out of the end it entered.

Sound amplification produced by four horn receivers of different flares and with ratios of end areas varying from 7.8 to 256 was roughly measured outdoors and also in a special room with sound-absorbing walls, using both a Rayleigh disk and a Webster phonometer. The amplifying factors found were from three to twenty times less than would be expected from the simple condenser theory, which is clearly untenable. It is concluded that the amplification is a result of both resonance and condensation.

PREVAILING THEORIES.

That the sound energy falling upon the ear or other form of sound receiver may be considerably increased by placing the receiver at the small end of a conical horn is a matter of common observation. The correct explanation of the amplifying action of the horn is quite another matter. In the opinion of the writer the complete explanation has not yet been given. Certain it is that the horn is not merely a condenser, nor is it merely a resonator. The former idea is the most common and the farthest from the truth. Doubtless many of us have thought of a conical horn as a sound condenser through which sound passes like liquid or shot through a funnel. Most textbooks that say anything at all about horns give substantially such an "explanation."

Quoting from one of the older books: "The reinforcing action of the ear trumpet has been attributed to the successive reflections of the sound waves, which multiplies their action on reaching the tympanum. But, as in the speaking trumpet, experiment has shown that the influence of the walls, and consequently the reflection of their inner surface, is very feeble, if any at all. The effect produced is in reality owing to the progressive diminution of the sections of the air surface which transmit the sound and which then transmit it with increasing energy towards the organ. This effect may be compared with that of a jet of water which issues from the orifice of a hose with much greater force than a body of water of equal diameter in the interior of the pump barrel."[1]

Quoting from one of the latest textbooks: "The ordinary speaking tubes connecting distant rooms in buildings depend not on regular reflection, but on the fact that the air particles next the inner surface of the tube vibrate most easily parallel with the surface; this causes the direction of vibration to be deflected by gradual bends in the tube, and consequently the wave runs along the tube without reflection. In ear trumpets, by the constraint of the smooth walls of the tube, the wave entering the wide end is gradually diminished in area till it emerges at the small end carrying all the energy that entered at the large end. Thus if the large end is 100 times that of the small end, *the energy per cubic centimeter* in the emergent wave is 100 times as great as in the wave which entered the trumpet, neglecting loss by friction, etc."[2] The redeeming word in this explanation is "etc."

Over against the notion that the horn is a condenser we have the statement that it is a resonator. "The effect of the horn is to reinforce the the vibrations which enter it due to the resonance properties of the air inclosed by the horn. . . . The horn is an air resonator . . . the response below the fundamental of the horn is very feeble."[3]

Quoting from the classic treatise of Lord Rayleigh:[4] "The case of progressive waves moving in a tube of variable section is also interesting. In its general form the problem would be one of great difficulty; but where the change of section is very gradual, so that no considerable alteration occurs within a great many wave lengths, the principle of energy will guide us to an approximate solution. It is not difficult to see that in the case supposed there will be no sensible reflection of the wave at any part of its course, and that the energy of the motion must remain unchanged . . . from which it follows that as the waves advance the amplitude of vibration varies inversely as the square root of the section of the tube. In all other respects the type of vibration remains absolutely unchanged. From these results we may get a general idea of the action of an ear trumpet. It appears that according to the ordinary approximate equations there is no limit to the concentration of sound producible in a tube of gradually diminishing section."

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[1] Guillemin, Application of Physical Forces, p. 114.

[2] A. L. Kimball, College Physics, Revised Edition, pp. 196–197.

[3] Dayton C. Miller, The Science of Musical Sounds, pp. 156 and 159.

[4] Lord Rayleigh, The Theory of Sound, Vol. II., p. 63.

In the light of the theory of reciprocity[1] it is difficult to harmonize the above statement with one by the same author a few pages later when speaking of the action of a trumpet. "From the theory of diffraction it appears that the sound will not fall off to any great extent in a lateral direction, unless the diameter of the large end exceed half a wave length. The ordinary explanation of the effect of a common ear trumpet, depending on a supposed concentration of the *rays* in an axial direction, is thus untenable."[2]

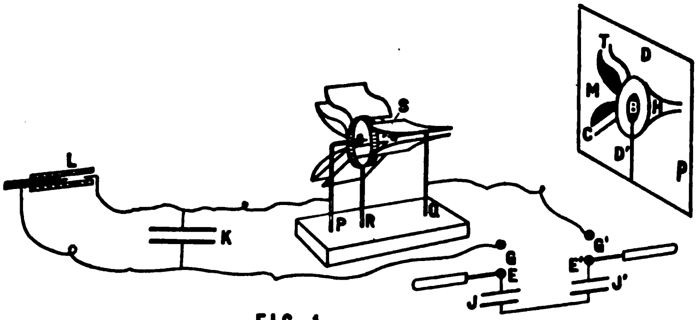

FIG. 1.

In view of such conflicting opinions, the writer decided to subject the question to experiment; by photographing sound waves passing through channels and by measuring the increase in intensity of a sound at a point when a conical horn is used as a "condenser."

Photographic Method.

Figure 1 is intended to show only the general principles of the photographic method used. Details of the light gap, "camera" box, spark control, etc., may be found in some of the writer's earlier papers.[3]

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[1] Ibid., Vol. I., p. 150.

[2] Ibid., Vol. II., p. 102.

[3] A New Method of Photographing Sound Waves, Phys. Rev., XXXV., Nov., 1912, p. 373.

J and J' are capacities, each of from one to five Leyden jars, averaging 525 cm. each, connected to the electrodes E and E' of an electric induction machine capable of producing sparks twenty to thirty centimeters long. The spark gaps G, G', S and L are in series. When the capacity J, J' is discharged through the gaps G, G', sparks pass at both S and L. The spark at S takes place between platinum terminals at the ends of the brass rods P and Q and produces a sound wave. By properly adjusting the length of the light spark L (1 to 3 cm.) and the capacity K (six to twenty Leyden jars), the light spark can be retarded until the sound wave produced by the sound spark at S has had time to travel a short distance radially outward from the axis of the sound spark. Then when the light spark occurs, it casts a shadow of the sound wave on the photographic dry plate P.[1] B is the shadow of hard rubber buttons placed on the rods at each end of the sound spark gap to minimize the fogging of the dry plate by the light from the sound spark.

In order to study the passage of sound waves between walls and plates, several plates were cut from sheet brass, and shaped and disposed about the sound spark as shown in the figure. The plates were supported by soldering them at one corner to a narrow brass ring, the ring being placed beyond the end of the spark gap so as to interfere but little with the wave produced by the sound spark. The rod R, supporting the ring, and the rods P and Q were placed in line with the light gap so that they cast but one shadow on the dry plate.

The writer was not very successful in photographing sound waves through transparent tubes and horns. The curvature of the walls of the tubes so interfered with the passage of the light through them that the waves could be photographed only at points along the axes of the tubes. The writer concluded, therefore, to curve some plates and so place them with respect to one another and to the sound spark axis that a vertical section at right angles to the spark axis would correspond to a longitudinal section of a tube or a horn. The shadow of plates so disposed, shown in Fig. 1, is the projection of such a section. Thus C represents a longitudinal section of a straight cylindrical tube, T a crooked tube, M a megaphone, and H a flared conical horn. For convenience they will be designated, respectively, straight tube, crooked tube, megaphone and horn. The spaces between the megaphone and the tubes on each side were closed to bring out more clearly their outlines. In the directions D and D' the wave was free to travel without interference from reflecting surfaces.

Except in so far as sound intensity affects sound velocity, it would appear that the shadow of a cylindrical sound pulse passing between plates curved and disposed as shown in the figure should represent a longitudinal section of a spherical pulse through tubes to whose longitudinal section the plate shadows correspond. Further, that the wave form in cylindrical tubes and horns for spherical pulses of the same radii as the cylindrical pulses would be obtained in the case of all but the crooked tube by rotating each system about its longitudinal axis.

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[1] Proc. Ind. Acad. Sci., 1915, p. 305.

It might be urged that we are dealing here with a sound pulse and not a sound wave. The writer[2] has shown that the velocity of such a pulse, except for points very near the spark axis, is the same as the velocity of a train of sound waves. Indeed, the pulse is more than a condensation only. In a study not yet published the writer has found that an electric spark produces both a condensation and a rarefaction and that the disturbed air shell near a spark is one wave length thick. But more to the point is the fact that the wave pictures show that the waves are exactly where we should expect them to be by Huygen's construction.

Figures 2 to 7, inclusive, show successive stages of an expanding spark wave, the average time interval between each of the six wave positions being about 0.00003 sec. Figure 3 is a double exposure, with a time interval of only 0.000006 sec. As would be expected, all six pictures show that the waves passed through the straight tube and megaphone without appreciable reflection, and that the megaphone wave suffered the greater attenuation. But on examining the waves through the crooked tube and through the horn we find convincing evidence that what has occurred is not just what some of us have been thinking would happen in such cases.

All the pictures show that there was energy reflection in every case except when the wave front was at right angles to the surface and the motion of the air parallel to the surface of the tube. In the case of the horn there was continuous reflection from one end to the other, even at the small end where the angle of the cone is very small. In the case of the crooked tube there were successive reflections. For the crooked tube, Fig. 6 and Fig. 7 show respectively an emerging and emerged wave much more attenuated than in the case of the straight tube of the same size. A considerable portion of the wave energy appears to be trapped inside the tube. However, it will be observed that the reflected waves in general were headed toward the outer end of the tube. This is not true, however, of the horn. Here the advancing wave shows unmistakable evidence of intensity increase or condensation, and that it emerged from the small end of the horn considerably amplified. But most of the energy was lost so far as the small end of the horn is concerned. The lost energy was contained in the reflected waves which, as the photographs show, headed the wrong way—"backing out" of the horn.

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[2] Proc. Ind. Acad. Sci., 1915, p. 299; 1918, p. 221. Phys. Rev., N.S., XVI., Nov., 1920, p. 449.

INTENSITY MEASUREMENTS.

Some sound intensity measurements substantiated what the photographs clearly suggest, that the condensing power of a horn is not the quotient of the areas of the two ends, that it is not even of the same order of magnitude in the case of horns of considerable angle.

The source of sound was an organ pipe blown by air from a tank in which a constant pressure was maintained by an electrically driven compressor. Intensity measurements were made with both the Rayleigh Disk[1] and the Webster Phonometer.[2] The intensity was measured at a given point, without horn. Then the horn was placed in position and the intensity measured again — at the same point. The quotient of the latter intensity by the former is called the amplifying power or amplification. If called the condensing power it should be remembered that it includes the amplification due to resonance.

The chief difficulty encountered in these measurements was due to reflection from the walls of the room. In a room 25 × 35 feet, except for certain well-defined interference regions, the sound was about equally intense everywhere and was practically the same when the receiving horn faced the source as when turned in the opposite direction. Then, too, the intensity was practically independent of the direction of the axis of the sounding organ pipe with respect to the receiving horn, and it varied but little with change of distance between source and receiver.

The apparatus was then set up out doors as far as possible from buildings, trees, and objects that would act as reflectors. The two chief sources of trouble outside were ground reflection and varying air currents. However, fairly consistent intensity measurements were obtained.

The most reliable results were obtained when the apparatus was set up in a double-walled, constant temperaure room in the basement of the physics laboratory. The room was practically sound proof for sounds originating outside. To reduce the reverberation the walls were covered with the material which could be had quickest and without expense. Amongst other things there were several hundred large gunny sacks and a number of lap robes, blankets and comforters. The absorption was by no means all that could be desired. But it enabled the making of measurements in substantial agreement amongst themselves and with those made out doors, and sufficiently reliable to disprove the statement that a horn is a condenser.

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[1] Rayleigh, Theory of Sound, Sec. 253b.

[2] Webster, Proc. Nat. Acad. of Sc., Vol. 5, May, 1919, p. 163. Ibid., July, 1919, p. 275.

PHYSICAL REVIEW, SECOND SERIES, VOL. XX.
December, 1922.

PLATE I.
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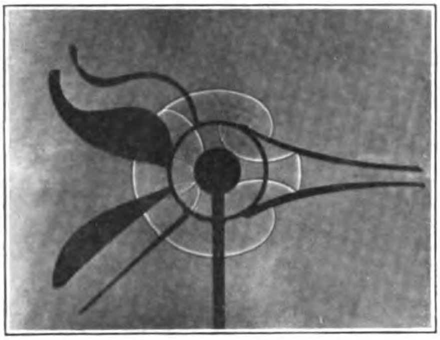

Fig. 2.

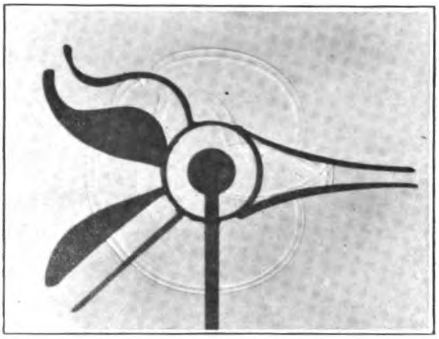

Fig. 3.

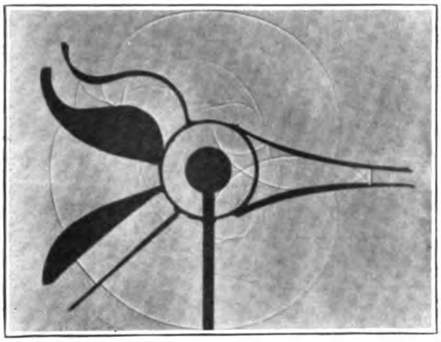

Fig. 4.

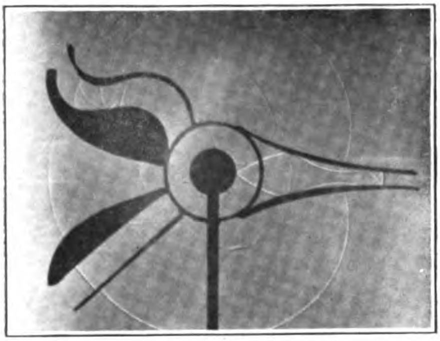

Fig. 5.

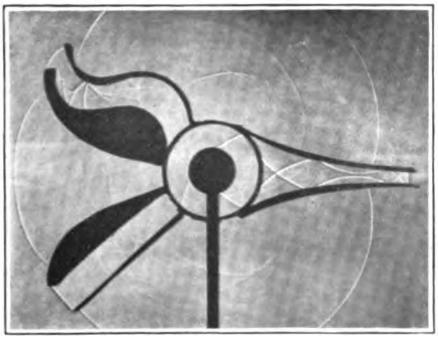

Fig. 6.

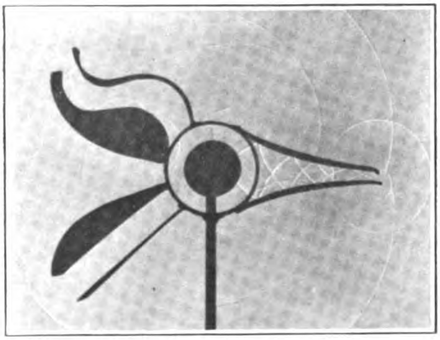

Fig. 7.

A. L. FOLEY.

Measurements were made with organ pipes of different pitch placed at different distances from the receiving apparatus. The horns used, four in number, were made of sheet zinc. All were thirty inches long when measured along the axis, and one and one quarter inches in diameter at the small end. The large end diameters were such that the ratios of the areas of the large and small ends were respectively 7.8, 33, 122, and 256.

Inasmuch as this experiment is to be repeated under wider and more favorable conditions than previously obtained, the writer will defer any extended publication and discussion of data. The following table, however, indicates the general character of the results:

Distance between Source and Receiver.	Ratio of End Areas of Horns.	Amplifying Factor.	
		By Rayleigh Disk.	By Webster Phonometer.
8.0 feet	7.8	3.1	2.9
8.0 "	33.0	7.9	4.3
8.0 "	122.0	11.9	6.0
8.0 "	256.0	13.0	7.3
6.5 "	7.8	2.6	2.0
6.5 "	33.0	9.1	4.3
6.5 "	122.0	10.3	6.0
6.5 "	256.0	8.3	6.5

The author attaches no importance to the data in the above table from the standpoint of their absolute values. There is no question, however, as to the order of the quantities involved. This being true, the condensing power of horns is not even approximately what it has been represented to be by many writers. For instance, if the "condenser" theory were true, the amplifying power of the larger horn should be 256 (neglecting friction — small in this case). The average of the four values given in the table is 8.8. The highest amplification obtained was 13, about one twentieth the theoretical value.

It will be noted that the intensity ratios given by the Rayleigh disk run higher than those given by the Webster phonometer. This may be due to the fact that the Rayleigh disk was suspended in free air — without resonator or enclosure — while the vibrating disk of the phonometer was mounted at the end of a cylindrical resonator. At such limited distances between source and receiver and with a sound as intense as that produced by an organ pipe (frequency 256), the phonometer was so sensitive it could not be used when its resonator was in tune with the source. Therefore, the phonometer was not used as designed to be used, with both disk and resonator in unison with the sound to be measured. The disk only was so adjusted.

The resonance theory of horn amplification requires that some of the energy of an emerging wave be reflected back into the horn. Figures 2 to 7 show that in the case of a spark wave the amount of the energy reflected at the open end of a pipe or horn is too small to give any trace of a reflected wave.

CONCLUSIONS.

1. The amplification of sound at the small end of a conical receiving horn is due to *both* resonance and condensation.

2. The amount of sound energy "condensed" at the small end of a conical horn receiver is but a small fraction of that demanded by the "condenser" theory. This theory is not tenable.

3. Sound pulses do *not* "glide around bends" in tubes and "slip" along slanting walls "without appreciable reflection." There is reflection at a surface whenever the molecules of air next the surface vibrate in any direction not parallel to that surface. Huygen's construction applies in every case.

4. Much of the energy of the waves reflected in a crooked tube of small angle may eventually emerge at the far end, but the several waves arrive at different times. Thus the form of the emerging wave may be widely different from that of the entering wave.

5. Much of the energy of a wave entering the large end of a conical horn is reflected and eventually *leaves the horn at the end it entered.* The wider the horn angle the greater the per cent. of energy thus "lost."

6. Of the energy of an emerging sound wave the per cent. reflected at the open end of a tube is small.

WATERMAN INSTITUTE FOR RESEARCH.
INDIANA UNIVERSITY.

AN EXPERIMENTAL INVESTIGATION OF THE DISPERSION OF A LIMITED WAVE TRAIN.

BY IRVIN H. SOLT.

SYNOPSIS.

Dispersion by a Prism of a Limited Train of Hertzian Waves, 7.8 and 9 cm. Long.—According to the theory developed by Sommerfeld, Brillouin, and Colby, some energy should be propagated through the prism undeviated, the proportion decreasing as the angle of incidence is increased. This conclusion has now been experimentally confirmed. To insure a large number of short wave trains, a pliotron circuit adjusted to a frequency of 170,000 cycles was used to energize a modified Righi vibrator consisting of two steel balls suitably mounted close together. The waves so generated were sent as a parallel beam through an opening in a wall to a 30° pitch prism, and the energy as a function of the angle of deviation was determined by means of a molybdenite crystal detector, in series with a sensitive galvanometer, placed at the focus of a parabolic mirror. Various possible sources of error were eliminated or corrected for. The undeviated energy was found to decrease from 26 per cent. for 0° incidence to 8 per cent. for 35° incidence, in general agreement with the theory.

Index of refraction of pitch for Hertzian waves, 7.8 cm. long, was found to be 1.99.

INTRODUCTION.

IN the neighborhood of an absorption band the index of refraction of a dispersing medium may be less than unity and consequently the velocity with which a given wave crest in a monochromatic wave train is propagated may exceed its velocity in vacuum. This is true only after the medium has reached a steady state, *i.e.*, theoretically, for an infinite wave train. From this one might conclude that a signal could be sent with a velocity greater than the velocity of light in vacuum in contradiction to the principle of relativity. A signal, however, must differ from an infinite monochromatic wave train in that it has some peculiarity of form, a beginning or an end, by means of which it can be identified. Sommerfeld[1] was the first to attack this problem theoretically, taking as his signal the limited sine wave

$$f(t) = \sin\frac{2\pi t}{P}, \qquad \text{for } 0 < t < T,$$
$$f(t) = 0, \qquad \text{for } t < 0 \text{ and } t > T,$$

incident perpendicularly on the dispersing medium. He expresses the signal in the form of a Fourier integral which represents the sum of an infinite number of infinite wave trains. Having done this he applies the ordinary dispersion theory and obtains an integral representing the disturbance, a distance x in the dispersing medium, as a function $f(t, x)$ of t and x, which he evaluates by Cauchy's method of integration in the complex plane. The result shows that in all cases, including the region of anomalous dispersion, the front of the wave train arrives at a point x in the medium in a time $t = x/c$ and consequently travels with vacuum velocity. The amount of energy which arrives at a given point with this velocity is very small and consists of waves which are very short compared with the incident radiation.

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[1] Sommerfeld, Ann. d. Phys., 44, p. 177, 1914.

The work of Sommerfeld was extended by Brillouin,[1] who treated the complex integration of the integral $f(t, x)$ more exhaustively. He defines the arrival of the signal as the moment when the amplitude of the disturbance reaches half its final value. Colby[2] investigated the case of oblique incidence, both with reference to form and direction of propagation of the first part of the disturbance. He showed that in this case also the wave front is propagated with vacuum velocity and is undeviated at the boundary. As time goes on the disturbance in the medium swings continuously toward the normal until the steady state is reached when it has the direction required by the ordinary law of refraction. The period of the first part of the disturbance is very short and the amplitude very small. Both quantities decrease with increasing obliquity, and increase as time goes on, the latter passing through a maximum and minimum before the steady state is reached.

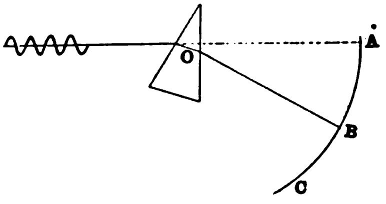

Fig. 1.

Consider now a wave train incident on a prism (Fig. 1). According to the theory outlined above, the front of the wave train will pass through the prism undeviated and arrive at the point A on the arc ABC. The succeeding part of the disturbance will arrive at consecutive points the emerging beam after the steady along AB, OB being the direction of state has set in. The disturbance which arrives at points between A and B is a transient effect which precedes the establishment of the steady state. It is the object of this investigation to detect this effect experimentally.

Since the effect we are investigating is very small and associated only with the beginning of a wave train, it is essential to use a source of radiation which emits a very large number of short wave trains per second. The limited sine wave assumed by Sommerfeld cannot be realized experimentally. The most convenient type of radiation to use is the highly damped wave emitted by a Righi vibrator. In this case most of the energy will be in the first period and hence the effect we are looking for will be a larger proportion of the total energy than would be the case if a longer wave train were used.

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[1] Brillouin, Ann. d. Phys., 44, p. 203, 1914.

[2] Colby, PHYS. REV., V., 3, 1915.

The Vibrator.

The source of radiation was a slightly modified form of Righi vibrator similar to the type frequently used in recent work[1] with short Hertzian waves. It consisted of two steel balls .95 cm. in diameter resting in sockets ground in a glass holder, or held between strips of wood. For an air gap and electric vector horizontal the holder shown partly in Fig. *2A* was used. It was made as follows: A piece of glass tubing 35 cm. long and .95 cm. in diameter was bent in the shape of a wide *U*, having vertical sides 8 cm. long. The horizontal portion was then bent into a loop until the vertical sides almost touched. A glass tube sealed to the under side of the loop serves as a support. It is fastened to a horizontal slider which makes it possible to adjust the balls accurately at the focus of the parabolic reflector. The gap between the balls was adjusted by means of a thin piece of glass forced between the two nearly parallel vertical portions of the holder.

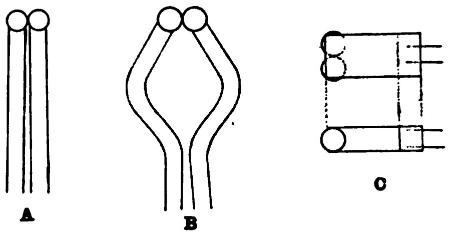

Fig. 2.
Different methods for holding vibrator.

When an oil gap was used the holder was similar to the above except that the vertical parts were bent out immediately below the balls, as shown in Fig. *2B*. This permitted the oil to flow away freely and reduced to a minimum fouling of the gap due to deposits of carbon from the decomposing oil. To keep the balls firmly seated it was necessary to connect the holder to a filter pump. Paraffine lubricating oil was contained in a reservoir above the reflector whence it flowed through a glass tube and issued from a capillary nozzle a few millimeters above the gap. The spent oil was caught in a receptacle immediately below the reflector, and was used repeatedly, being filtered occasionally to remove the carbon.

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[1] Webb and Woodman, Phys. Rev., XXIX., p. 89, 1909; Woodman and Webb, Phys. Rev., XXX., p. 561, 1910; Severinghaus and Nelms, Phys. Rev., I., p. 411, 1913; and others.

Some observations were made with the electric vector vertical. In this case the two balls were held between two thin strips of wood, 1.7 cm. by 2.8 cm., one end of which was glued to a piece .9 cm. square and 1.7 cm. long (Fig. 2*C*). A glass rod waxed to the latter served as a support.

The leads to the vibrator consisted of brass wire 2 mm. in diameter passing through ebonite bushings in the reflector immediately behind the vibrator. The ends were rounded off and a short piece bent over 45°.

The reflector was a sheet of silver-plated copper in the form of a paraboloid of revolution, having an aperture 50.8 cm. in diameter, a depth of 13.8 cm. and a focal length of 11.4 cm. It was mounted on a rigid stand with its axis horizontal and 155 cm. above the floor.

As pointed out above, it is necessary that the vibrator emit a large number of wave trains per second. To satisfy this condition the alternating potential used to excite the vibrator must have as high a frequency as possible. At first a 10-in. induction coil operating on 60 volts and a mercury jet interrupter giving about 900 interruptions per second were employed. The oil gap already described was used with this coil. It was necessary to regulate the current through the gap by means of a large water resistance in series with the secondary of the induction coil. When this was not done the gap readily fouled and the vibrator became very erratic.

The observations taken with the induction coil will be discussed later. They indicated the existence of the effect, but the galvanometer deflections for small deviations were only a few millimeters. It was therefore desirable to replace the induction coil by some device which would give a higher frequency. This was accomplished by means of the pliotron circuit shown in Fig. 3. The essential features of this circuit are a large inductance and a small capacity.[1] The inductances L_1, L_2 were about 5 millihenries each wound in four

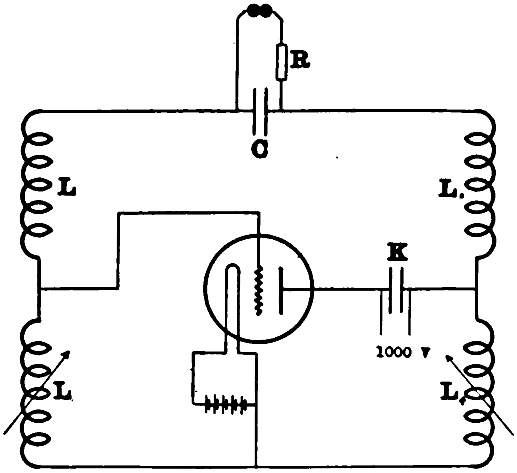

Fig. 3.
Pliotron circuit.

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[1] W. C. White, Gen. Elec. Rev., Aug., 1917.

units. Each unit consisted of from 60 to 75 turns of No. 20 wire diameter and 20 cm. long. L_3 and L_4 were of wound on a wooden polygonal frame, the winding being 30 cm. in the variometer type, the settings being usually about .1 and .5 millihenry respectively. The condenser C consisted of two sheets of tin 45 cm. by 50 cm. supported on four glass rods passing through holes near each corner, and separated by pieces of glass tubing 10 cm. long fitting over the glass rods. The water resistance R was necessary to prevent the oscillatory discharge of the condenser C, through the circuit containing the vibrator. Two type P pliotrons were used in parallel. At the frequency employed (170,000) the energy emitted by a vibrator with an oil gap is no greater than with an air gap; since the sparks pass so rapidly that a bubble of vapor is always in the gap. Consequently the air gap described above was used exclusively. In this connection it is interesting to note that Bartenstein[1] and Lindmann[2] used a Tesla transformer to excite a vibrator partially or totally immersed in oil. It is doubtful whether the presence of the oil in this case increased the energy emitted by the vibrator except in so far as it increased the wave-length.

The adjustment of the circuit was somewhat critical. The tendency of the spark gap was to emit a musical note, indicating that the oscillations in the pliotron circuit died down after each spark and required a large number of cycles to be built up sufficiently for another spark to pass. With proper adjustment the spark made a noise resembling that due to a blast of air from a fine nozzle.

THE RECEIVER.

The type of receiver most commonly used for quantitive work with electric waves has been that devised by Klemenčič.[3] It consists of two narrow copper wings joined together by a thermocouple which is connected to a sensitive galvanometer. For maximum sensitivity the galvanometer must be of the low resistance, moving magnet type which is frequently tedious to work with. Sjöström[4] has recently described a crystal detector which he claims is more sensitive than the thermocouple type, besides having the advantage of high resistance. The receiver used in the present work was a modified form of the type developed by Sjöström. A cross section of it is shown in Fig. 4.

Two brass rods b, b', 10 cm. long and .5 cm. in diameter, screw into brass cylinders c, c', which are held in an ebonite cylinder a. The hole in the cylinder *c* ends in a shoulder against which a thin flake of molybdenite *d* is pressed by the rod *b*. The rod *b'* ends in a blunt point which makes contact with the flake. A glass tube *e*, 40 cm. long, serves as a holder. The galvanometer leads are soldered to *c*, *c'*, closely twisted and passed through the glass tube. The main receiver was placed at the focus of a parabolic reflector having the same dimensions as that used with the vibrator and mounted on a stand the same height above the floor.

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[1] Bartenstein, Ann. d. Phys., 29, p. 201, 1909.

[2] Lindmann, Ann. d. Phys., 38, p. 523, 1912.

[3] Klemenčič, Wied. Ann., 42, p. 416, 1891.

[4] Sjöström, Diss. Upsala, 1917.

The resistance of such a receiver is high, of the order of several thousand ohms. This fact makes it possible to obtain high sensitivity using a d'Arsonval galvanometer. Two high sensitivity moving coil galvanometers made by the Leeds and Northrup Company were used. The one connected to the main receiver had a sensitivity of 2.5×10^{-10} ampere and a period of 8.5 seconds, while that connected to the check receiver had a sensitivity of 5×10^{-10} ampere and a period of 6 seconds.

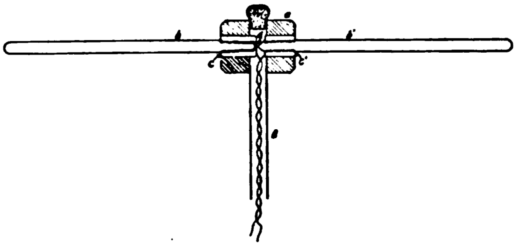

Fig. 4.

The receiver.

THE PRISM.

The dispersing medium was a pitch prism with a refracting angle of 30°. The faces were 75 cm. high and 85 cm. long. It was cast in a wooden box which was retained throughout the work. The sides of the box were made separately of 1-in. yellow pine boards, being held together by two bolts at each vertical edge.

ARRANGEMENT OF THE APPARATUS AND METHOD OF OBSERVATION.

The final arrangement of the apparatus is shown in Fig. 5. The oscillating system *S* and the check receiver *C* were in one room, while the prism *P*, the main receiver *M* and the galvanometers *G* were in an adjacent room. The radiation passed through an aperture 50 cm. in diameter in the center of a metallic screen *A* about 270 cm. square covering the doorway and adjacent part of the wall. In the doorway, between this screen and the prism was a cylindrical screen *B*, 50 cm. in diameter and 100 cm. long. The object of the screening is to let no radiation enter the room in which the main receiver is located except that which passes through the prism.

The prism was mounted on a turntable which permitted a rotation of 40°, the axis of rotation intersecting the axis of the parabolic mirror at *S*. The mounting was adjusted so the angle of incidence could be varied from 0° to 40°, and the prism was placed as close to the screen *B* as the maximum angle of incidence permitted.

The distribution of energy in the spectrum produced by the prism was measured by moving the main receiver along the arc of a circle *D* having a radius of 200 cm., the axis of the receiving mirror always intersecting the axis of rotation of the prism. To take account of the variation of the energy emitted by the vibrator a check receiver *C* was employed. It was located about 100 cm. from the vibrator and just out of the beam of radiation passing through the aperture in the screen *A*.

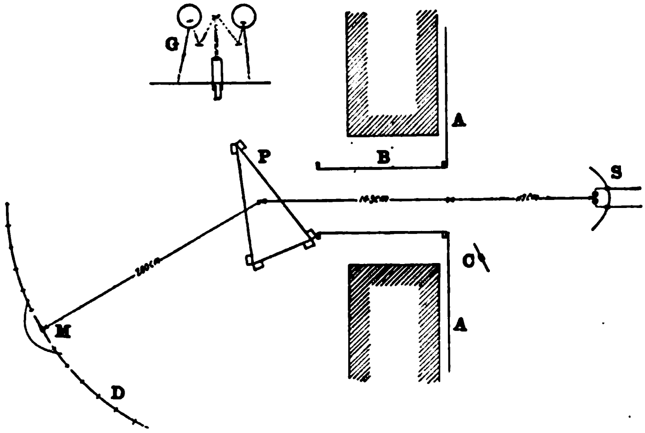

Fig. 5.

The two galvanometers were located side by side on a wall bracket (*G*, Fig. 5). The same scale served for both, and by means of a system of mirrors the deflections of both were read simultaneously in the same telescope. The exciting source of the vibrator (induction coil or pliotron circuit) was controlled by strings passing through the wall. Thus all the observations could be made by one observer.

The energy emitted by the vibrator at any given instant was assumed to be proportional to the deflection of the galvanometer connected to *C*. The relative energy received at any point of the circle *D* was therefore proportional to the ratio of the deflection of *M* to the deflection of *C*. Several readings were taken for each setting of *M* and the average value of M/C used. With increasing age of the vibrator the ratio M/C did not always remain constant, but generally decreased more or less irregularly. Consequently, frequent readings were taken with the main receiver in some chosen position on the circle D. If M/C varied the other readings were corrected, *i.e.*, the energy received at the various points along D was expressed in terms of the energy received at the reference position.

The possible sources of error in the present work are the following:

1. Effect of the box surrounding the prism.
2. Radiation penetrating the walls beyond the screen A.
3. Radiation reflected from the walls, floor and ceiling of the room in which the observations were made.
4. The disturbing influence of the induction coil and pliotron circuit.

The boards which formed the faces of the prism were quite uniform and free from knots. No disturbance could be expected from them. The only course of disturbance in the box was scattering by the bolts and screws at the vertical edges. The nearest that any of the bolts approached to the geometrical edge of the beam, measured from the edge of the screen B and in a place containing the axis of B, was 15°. If we substitute $\theta = 15°$, $\lambda = 7.8$ cm., $R = 25$ cm. in the formula

$$\text{Sin } \theta = \frac{m\lambda}{\pi R}$$

for the diffraction pattern, we find $m/\pi = .83$, which corresponds to the second maximum.[1]

Now the intensity of the second maximum is .017 times the intensity of the central maximum. Furthermore, not more than two of the bolts ever approached as close as 15° at one time, and all the screws were farther removed than the bolts. From this it appears that no appreciable error could have been introduced by the box surrounding the prism. To investigate this point further some observations were made with the frame removed. In this condition the prism rapidly lost its shape, but enough readings could be taken to show that the frame caused little trouble compared with the total effect observed.

The disturbance due to radiation penetrating the wall between the two rooms could readily be determined by noting the deflection of M when the aperture in A was closed by a screen. This was made very small by making A sufficiently large.

Although the room in which the observations were made was large (9.5 m. long, 8.5 m. wide, and 4 m. high), there was nevertheless an appreciable disturbance due to reflection from the walls, etc., which could not be eliminated. Its magnitude was determined by making observations with a screen 85 cm. square interposed between the prism and *M*, near the former and perpendicular to the axis of the receiving mirror. The correction thus obtained included also (2) and to a certain extent (1). It was applied to all the observations made. If the vibrator was erratic, as was frequently the case toward the end of a series of observations, the readings for any given position of *M* were taken alternately with and without the screen. The average value of M/C with the screen was subtracted from the average value of M/C without the screen and the result taken as the true relative energy for that position of *M*.

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[1] Wood's Physics Optics, p. 237.

The disturbance due to the exciting source consists of two parts: radiation from the leads to the vibrator and induced currents in the galvanometer leads. To determine whether radiation from the leads caused any trouble the vibrator was removed from its holder and the leads brought together making a spark-gap in air a few millimeters long. If this gap was much less than 3 mm. it was difficult to get rid of radiation. In all the work the side gaps in air between the leads and the vibrator were never less than 3 mm. In the case of the induction coil the radiation effect was eliminated by making the leads short and enclosing them in red fiber tubing. This material is a very poor dielectric at high frequencies and consequently helped to damp out the oscillations in the leads. The radiation effect in the case of the pliotron circuit was due to the oscillatory discharge of the condenser *C*, Fig. 3. This was readily eliminated by making the water resistance *R* sufficiently large.

As Sjöström[1] has observed, some receivers seem to be more sensitive to induced currents in the galvanometer leads than others. Trouble due to this cause was entirely confined to the check receiver when the pliotron circuit was used. By properly choosing the receiver and closely twisting the galvanometer leads it could be eliminated or at worst made very small.

After the apparatus was finally adjusted no disturbance due to the exciting source could be detected in the main receiver, while the effect on the check receiver, if it existed at all, was small and fairly constant. Since we are only interested in the relative values the inaccuracy introduced by a small constant error in the deflections of the check galvanometer is negligible.

RESULTS.

The energy distribution under various conditions is shown graphically in Figs. 6 and 7. The abscissæ are deviations in degrees measured from the direction of the incident beam. The ordinates are energy expressed in per cent. of the maximum. With this system of coördinates the various curves are qualitatively comparable. The curves in Fig. 6 were taken with a vibrator consisting of .95 cm. spheres with an oil gap, excited by an induction coil. They confirm the theory qualitatively in that they show that some energy passes through the prism undeviated and that this effect decreases with increasing angle of incidence.

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[1] Loc. cit., p. 26.

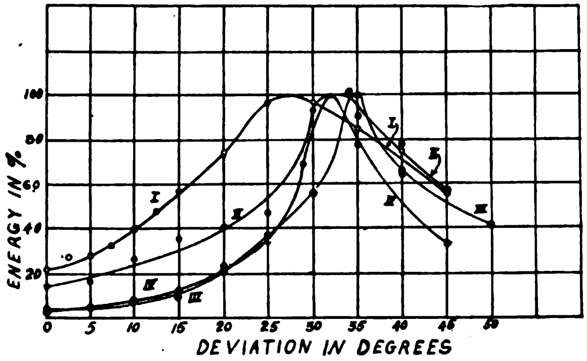

Fig. 6.

Spectral distribution of energy emitted by .95 cm. vibrator with oil gap.

I. Angle of incidence 0°
II. " " " 15°
III. " " " 24°
IV. " " " 32°

From curve IV., Fig. 6, it is seen that minimum deviation for the maximum in the energy curve occurs at 32° from which the index of refraction of pitch is found to be 1.99. This is much larger than the value 1.67 found by Hertz for waves about 60 cm. long.

Curves I. and II., Fig. 7, were obtained with a .95 cm. vibrator in air with the electric vector perpendicular to the refracting edge of the prism. They are much flatter than the corresponding ones for the oil gap and induction coil. This is due to the fact that the vibrator in air emits a more highly damped wave than in oil, so that a larger percentage of the total energy passes through the prism before the steady state is established. Figure 8 shows the variation of the energy which passes through the prism undeviated, with the angle of incidence. In this case the main receiver was kept fixed in the position of no deviation while the prism was rotated. The deflection of the main galvanometer for 0° incidence was 8.2 cm. and with the prism removed, 30.5 cm. With a screen interposed in the manner described the deflection was .2 cm.

Curve III., Fig. 7, shows the energy distribution for 32° incidence with a .95 cm. vibrator arranged so that the electric vector was parallel to the refracting edge. It differs from II. in that it has a more distinct maximum. The undeviated energy was less than 2 per cent. of the incident energy as compared with 10 per cent. when the electric vector was perpendicular to the refracting edge. This is partly due to the difference in orientation of the receiver in the two cases. With the electric vector horizontal, *i.e.*, perpendicular to the refracting edge, the receiver was also horizontal and subtended an angle of about 6° at the axis of rotation of the prism. It was 20 cm. long and consequently energy brought to a focus a distance of 10 cm. on either side of the geometrical focus of the mirror was caught by the receiver. When the receiver was vertical it caught little energy except that which was brought to a focus at the geometrical focus of the mirror. We should also expect a difference in the two cases in the direction observed since in the steady state the component of the electric vector in the plane of incidence is more readily transmitted than that perpendicular to the plane of incidence.

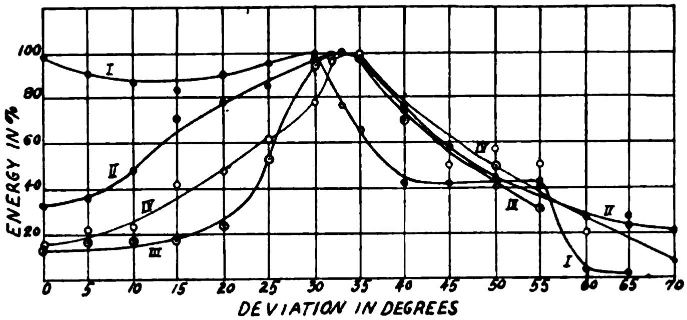

Fig. 7.

Distribution of energy emitted by vibrator with air gap.

I. Angle of incidence 0°, vibrator consisting of .95 cm. spheres.

II. Angle of incidence 32°, vibrator same as I.

III. Angle of incidence 32°, vibrator consisting of two .95 cm. spheres mounted with axis parallel to the refracting edge of the prism.

IV. Angle of incidence 32°, vibrator consisting of two 1.52 cm. spheres mounted with axis perpendicular to refracting edge of prism.

Curve IV., Fig. 7, shows the distribution of energy for 32° incidence using a 1.52 cm. vibrator in air mounted horizontally. The general shape of the curve is the same as in the corresponding case with the smaller vibrator. The deflections were very erratic beginning at 45° which accounts for the irregularities at 45° and 60°.

A few observations were made with a .61 cm. vibrator in air but the deflections were too small to be of much value. It does not seem feasible to use vibrators as small or smaller than this without some means of increasing the energy emitted. This might be accomplished by enclosing the vibrator in a glass bulb either exhausted to a very low pressure or filled with some gas at a pressure of several atmospheres. In the latter case the decreased mobility of the ions would tend to set an upper limit to the useful frequency of the exciting source.

WAVE-LENGTH MEASUREMENTS.

The wave-length of the radiation emitted by the vibrator was measured by the Boltzmann mirror interference method first used by Klemenčič and Czermak.[1] In this method the energy from the vibrator arrives at the receiver after reflection from a mirror which is divided into two halves, so that the line of separation is in the plane of incidence. By separating the two mirrors thus formed, interference between the two halves of the beam takes place at the receiver. Each mirror consisted of a sheet of plate glass 35 cm. by 70 cm. covered with tinfoil, one was fixed and the other mounted on the carriage of a dividing engine. The wave-length is the distance between two successive maxima or two successive minima. For the .95 cm. spheres in air the wave-length was 7.8 cm. and for the 1.52 cm. spheres in air about 9 cm. In the latter case the maxima and minima of the interference curve were so flat that it was difficult to determine the wave-length accurately. These values indicate pronounced "mirror-action." [2]

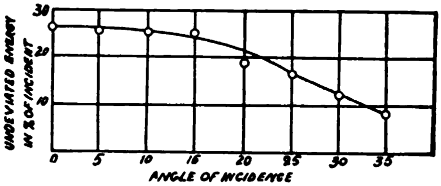

Fig. 8.

The nature of this phenomenon is not very well understood. The size and shape of the collecting mirrors somehow influence the wave-length of the radiation. When the focal length is comparable to the wave-length the emitted beam has a more or less definite wave-length which is determined by the geometry of the mirror and not by the size of the vibrator. For the present purpose it is not essential that the vibrator emit its characteristic wave-length; all that it is desirable to know is what it actually does emit.

The theory indicates that the wave-length of the undeviated energy is very short and the intensity very weak compared with the incident radiation. From this it appears that the effect observed is not due to strictly undeviated energy—*i.e.*, the disturbance called the "first forerunners" by Brillouin, but to energy that has undergone slight deviation. This view is strengthened by a consideration of the finite size of the receiver. An attempt was made to investigate the wave-length of the energy received in the neighborhood of zero deviation by means of the interferometer. No evidence of interference could be obtained. This was probably due to the fact that the energy reflected from the interferometer was not sufficiently monochromatic, since the wave-length depends upon the thickness of the medium traversed and consequently varies continuously from the refracting edge to the base.

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[1] Weid. Ann., 50, p. 177, 1893.

[2] Webb and Woodman, loc. cit., p. 100. These investigators found 6.7 cm. for the characteristic wave-length of a .95 cm. vibrator with an oil gap.

The author takes pleasure in expressing his thanks to Dr. E. F. Nichols, who suggested the problem and method of solution, and to Professor L. Page, for advice concerning questions of theory. His thanks are also due Mr. G. C. Southworth, for advice on the construction and manipulation of the pliotron circuit.

Sloane Laboratory,
Yale University,
New Haven, Conn.

NOTE ON MUSICAL DRUMS.

By R. N. Ghosh.

Synopsis.

Vibration of Symmetrically Loaded Circular Membranes.—In India there are musical drums which are loaded over a central zone in such a way as to give harmonic partials. The *theory* is presented for two cases, namely when the load varies inversely as the first power and as the second power of the distance from the center. It is found that in the second case the partials form a harmonic series, whereas in the first case they do not.

In India there are many musical drums like kettledrums which are used in company with stringed instruments. They differ from kettledrums in two respects, (1) they are loaded over a central zone; (2) they elicit harmonic partials.[1] It is well known that the partials of an unloaded circular membrane do not form a harmonic series, and a few of them give a consonant chord. From a look at the Indian instruments it becomes evident at once that the load per unit area varies as we proceed outward from the center. The investigation of the nature of the vibration when the load varies inversely (1) as the first power, and (2) as the second power of the distance from the center, can be effected very simply, but the writer could not find any mention of it in the textbooks.

The equation of motion in the case of circular membrane is given by

$$\rho\frac{d^2\omega}{dt^2} = T_1\left\{\frac{d^2\omega}{dr^2}+\frac{1}{r}\frac{d\omega}{dr}+\frac{1}{r^2}\frac{d^2\omega}{d\theta^2}\right\},$$

where the symbols have their usual meaning. Assume $\omega \propto \cos(kct)$ and

$$\rho = \frac{\rho_0}{r}. \tag{1}$$

Put $T_1/\rho_0 = c^2$ and further assume $\omega = v\cos(n\theta)$, then v must satisfy

$$\frac{d^2v}{dr^2}+\frac{1}{r}\frac{dv}{dr}+\left(\frac{k^2}{r}-\frac{n^2}{r^2}\right)v = 0. \tag{2}$$

Put $x = 2k\sqrt{r}$, then (2) becomes

$$\frac{d^2v}{dx^2}+\frac{1}{x}\frac{dv}{dx}+\left(1-\frac{4n^2}{x^2}\right)v = 0. \tag{3}$$

$$\therefore\quad v = AJ_{2n}(x) = AJ_{2n}(2k\sqrt{r}).$$

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[1] Nature, Jan. 15 (1920), p. 500.

If at $r = a$ the membrane is fixed we must have $J_{2n}(2k\sqrt{a}) = 0$ giving real values of k. The nature of these roots is well known, they do not from a harmonic series. The effect of the variation in density is mainly upon the absolute pitch of the vibrating membrane.

$$\text{Case II} \quad \rho = \frac{\rho_0}{r^2}. \tag{4}$$

Let us consider the simple case of symmetrical vibrations only, so that (2) becomes

$$\frac{d^2v}{dr^2} + \frac{1}{r}\frac{dv}{dr} + \frac{k^2}{r^2}v = 0. \tag{5}$$

$$\therefore \quad v = A \cos(k \log r). \tag{6}$$

The boundary condition gives

$$\cos(k \log a) = 0.$$

$$\therefore \quad k \log a = (2n + 1)\frac{\pi}{2}. \tag{7}$$

The partials now form a series of odd harmonics, and the absolute pitch is also disturbed.

Muir Central College,
Allahabad, India,
July, 21

ACOUSTIC WAVE FILTERS.

By G. W. Stewart.

Synopsis.

Acoustic Wave Filters Composed of a Series of Like Sections.—(1) *Theory.* Taking the impedance of any part of an acoustic circuit to be equal to the complex ratio of the applied pressure difference to the rate of change of volume displacement, it is shown that, neglecting dissipative forces, it is possible to construct a filter having limiting frequency values of no attenuation determined by the formulæ $Z_1/Z_2 = 0$ and $Z_1/Z_2 = -4$, where Z_1 is the impedance of the transmitting conduit circuit and Z_2 of each branch of each section. The impedance of any section depends on the inertance M of dimensions mass per unit area squared, and the capacitance C which has the dimensions of stiffness per unit area squared. If M and C are in parallel, $Z = iM\omega/(1 - MC\omega^2)$, whereas if they are in series, $Z = i(M\omega - 1/C\omega)$. For instance, in the case of a closed chamber or resonator, M and C are in series and are equal to ρ/C and $V/\rho a^2$ respectively where ρ is the density of the medium, c is the conductivity of the mouth, a the velocity of sound and V the volume. Formulæ are derived for various assumed cases. On account of the uncertainty as to whether a tube may be considered sa having the equivalent inertness and capacitance connected in parallel or in series, the application of these formulæ to actual cases is somewhat empirical. (2) *Construction and test of filters of three types.* Low-frequency-pass filters were made, for example, by two concentric cylinders joined by walls equally spaced and perpendicular to the axis. Each chamber thus formed had a row of apertures in the inner cylinder which served as the transmission tube. In one case the volume of each chamber was 6.5 cm.^{3}, the radius of the inner tube 1.2 cm. the length between apertures, 1.6 cm. A chamber and one such length of the inner tube is called a section. Four such sections were found to transmit 90 per cent. of the sound from zero to approximately 3,200 d.v. where the attenuation became very high, resulting in zero transmission up to about 4,600 d.v. where transmission again appeared, Other similar filters of different dimensions attenuated through wider or narrower ranges. The lower limit of attenuation was found to correspond within 8 per cent. with the formula: $f = (1/\pi)(M_1C_2 + 4M_2C_2)^{-1/2}$. The upper limit was not predicted theoretically. High-frequency pass filters were made with a straight tube for transmission and short side tubes, for example, 0.5 cm. long and 0.28 cm. in diameter, opening through a hole with conductivity 0.08 into a tube 10 cm. long and 1 cm. in diameter. Six sections of such a filter would transmit about 90 per cent. of sounds above 800 but would refuse transmission to sounds of lower frequency. As would be expected, the cut off is not sharp. Filters with other dimensions were found to have an upper limit of attenuation varying from 450 to 2,300 d.v., agreeing with the formula $f = (1/2\pi)(1/4M_2C_1 + 1/M_1C_2)^{1/2}$, within about 13 per cent., on the average. The single-band filters made were a combination of the other two types, having side tubes leading to chambers of considerable volume. For instance, three sections each 5 cm. long and 0.5 cm. in diameter, with side tubes of the same size and 2.2 cm. long leading to a volume of 28 cm.^{3}, transmitted between 270 and 370 d.v. The frequencies of the edges of the band of small attenuation are determined by the following formulae,

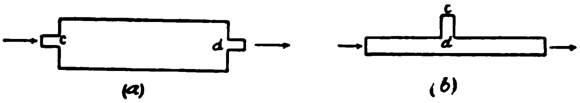
$$2\pi f = [M_2C_2(1 + M_2'/M_2)]^{-\frac{1}{2}} \text{ and}$$

$$2\pi f = [M_2C_2(1 + 4M_2/M_1)^{-1}(1 + M_2'/M_2 + 4M_2'/M_1)]^{-\frac{1}{2}}. \quad \text{Such filters}$$

exhibit the same variations from theoretical performance as would be expected from a combination of the other two types. However, the agreement of each type with theory is sufficient to enable filters to be designed to fulfill set conditions. The *attenuation secured* with only four sections is very great, the transmission being certainly less than 10^{-7} in the attenuated region, while it may rise to 90 per cent. in unattenuated regions. *Possible applications* of these simple filters in laboratory work and in connection with specking devices, are briefly suggested.

I. General Introduction.

THE selective transmission of an acoustic wave of a given frequency is well known. A Helmholtz resonator with a small ear opening is such a filter. Cylindrical tubes such as shown in Fig. 1 will also serve as filters, (*a*) transmitting chiefly the resonating frequencies of *cd* and (*b*) giving poor transmission especially for the resonating frequencies of *cd*. The acoustic wave filters which this article describes are different in principle and in performance in that they do not depend upon resonance itself, but upon the interaction between recurrent similar sections of a transmission "line," these sections containing the elements upon which free vibrations are to depend, and having over-all dimensions that are small in comparison with a wave-length of the sound.



(*a*) (*b*)

Fig. 1.

These new filters are remarkable in that selected groups of frequencies, extending over a large range, can be eliminated in the transmission. Up to the present time, three kinds have been constructed and tested. The low frequency pass filter will give approximately zero transmission at all frequencies above, and a fairly good transmission below a certain predetermined frequency. The high-frequency filter will transmit above a minimum frequency. The single-band filter will transmit a group of frequencies. In all cases, the frequency limits are ascertained approximately by calculation from the dimensions so that the filters may be designed to fit specifications. In these filters, the cutoffs are not sharp and the performances are not exactly as just stated, but, as will be shown, the explanation is found in the fact that the experimental conditions only approximate the theoretical.

II. Theory.

A. General.

An exact theoretical discussion of the acoustic wave filter may be possible, but certainly there is much to be gained in securing a theory which, though only approximate, will aid in understanding the operation of the filters and in developing new designs. The well-known electric wave filters suggested to the writer the possibility of analogous effects in acoustics. Naturally, the theory[1] of the electric filters has been of much assistance.

Certain limitations will be imposed in our discussion. We will assume that the length of any selected section of an acoustic "line" or conductor is so small in comparison with a wave-length that no change in phase occurs therein. We will consider only sinusoidal waves. The term "acoustic impedance" will be used. Its absolute value is the ratio of the maximum pressure difference applied to the maximum rate of change of volume displacement. When complex notation is used for simplicity, as in alternating electric current theory, the acoustic impedance is the complex ratio of the pressure difference applied and the rate of change of volume displacement. The mathematical procedure will be based upon three hypotheses which are obviously reasonable approximations. They are: (1) the rate of volume displacement in any selected portion of the line, with a harmonically varying applied difference of pressure, can always be expressed by $Ie^{i\omega t}$ where I is complex; (2) the product of acoustic impedance and rate of volume displacement in any selected portion of the line equals the difference of pressure applied; (3) the algebraic sum of the volume displacements at any junction of lines is zero. By acoustic "line" is meant a bounded region of fluid or solid, forming a tube or channel and capable of transmitting sound waves in the direction of the tube or channel only.

We will consider an acoustic wave filter consisting of equal acoustic impedances in series, divided into sections by acoustic impedances in what might be termed shunt branches. In Fig. 2, let a sound wave of a frequency $\omega/2\pi$ be transmitted through the line AG, a portion of an infinite line, containing a series of equal impedances, Z_1. Let each branch line AB, CD, EF, GH, etc., contain an impedance Z_2 and terminate in a

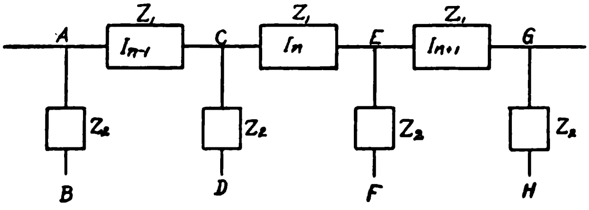


Fig. 2.

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[1] U. S. Patent 1,227,113 by George A. Campbell. Chapter XVI. of Pierce's "Electrical Oscillations and Electric Waves," 1920.

volume of gas otherwise at rest, so that there is a common constant pressure at or near these termini. Let $I_n e^{i\omega t}$, etc., represent the rates of change of volume displacement in the corresponding lines, I_n being a complex quantity, and let the positive direction be from A to G. From the three conditions stated in the foregoing paragraph the following equation may be secured:

$$Z_2(I_{n-1} - I_n) = Z_2(I_n - I_{n+1}) + Z_1 I_n$$

or

$$I_{n+1} - \left(2 + \frac{Z_1}{Z_2}\right) I_n + I_{n-1} = 0. \tag{1}$$

This equation does not require an infinite line, but we will for convenience impose that condition. We may then write, using ΔP as the complex pressure difference over a branch,

$$\Delta P_{CD} = I_n(Z_1 + Z_\infty)$$

and

$$\Delta P_{BF} = I_{n+1}(Z_1 + Z_\infty),$$

wherein Z_∞ is the impedance of the infinite network to the right in the figure and has the same value in both equations.[1] Substituting the values,

$$\Delta P_{CD} = Z_2(I_{n-1} - I_n),$$
$$\Delta P_{BF} = Z_2(I_n - I_{n+1})$$

and dividing we have,

$$\frac{I_{n+1}}{I_n} = \frac{I_n - I_{n+1}}{I_{n-1} - I_n}$$

or

$$\frac{I_{n+1}}{I_n} = \frac{I_n}{I_{n-1}}. \tag{2}$$

Let us call the ratio of these successive I's, e^Y, where Y is unknown but in general is complex. Substitute in (1), and we have,

$$e^Y + e^{Y-} = 2 + \frac{Z_1}{Z_2}$$

or

$$\cosh Y = 1 + \tfrac{1}{2}\frac{Z_1}{Z_2}. \tag{3}$$

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[1] The filter through its branches terminates in the undisturbed medium. The pressure at E can be expressed by $I_n Z_\infty$. From the equation of motion of a portion of a vibrating medium having a sinusoidal impressed force, and possessing mass, stiffness and dissipation, it can readily be shown that the impedance Z is a function of mass, stiffness, the dissipative factor and frequency only. In as much as these factors are the same for our Z_∞, whether taken from E or from G or any junction point, the assumption of identity of the Z_∞'s is justified.

If Y is a pure imaginary the rates of volume displacement in two adjacent sections differ only in phase. If Y is not a pure imaginary the rate of volume displacement is diminished in transmission, obviously the diminution occurring away from the input end. If Y is a pure imaginary, since cosh $ix = \cos x$

$$+1 > \left(1 + \frac{1}{2}\frac{Z_1}{Z_2}\right) > -1 \tag{4}$$

and hence the limiting values of no attenuation are determined by the following:

$$\frac{Z_1}{Z_2} = 0, \tag{5}$$

$$\frac{Z_1}{Z_2} = -4. \tag{6}$$

We can find the limiting values of no attenuation in a filter by utilizing the actual values of Z_1 and Z_2. It would therefore appear that an acoustic wave filter can be constructed, the only uncertainty being the manner of constructing Z_1 and Z_2. In order to determine upon the practical development of the filter, idealized conditions will first be discussed.

B. Inertance and Capacitance in Parallel.

Consider two idealized diaphragms, a and b, supposed to move as a whole, the former having mass, m_a, and not stiffness, and the latter stiffness, f_b, and not mass. Let them have areas S_a and S_b and displacements ξ_a and ξ_b and let them be connected in parallel as branches of an acoustic line so that they are subject to the same fluid pressure differences, $Pe^{i\omega t}$. Then,

$$m_a\frac{d^2\xi}{dt^2} = S_aPe^{i\omega t} \qquad \text{and} \qquad f_b\xi_b = S_bPe^{i\omega t},$$

the latter being merely the definition of f_b.

If we are concerned with the total volume displacement of the gas at the diaphragms, X_a and X_b, these equations become:

$$\frac{m_a}{S_a^2}\frac{d^2X_a}{dt^2} = Pe^{i\omega t} \qquad \text{and} \qquad \frac{f_bX_b}{S_b^2} = Pe^{i\omega t}. \tag{7}$$

We wish to obtain an expression for dX/dt or the rate of change of volume displacement in the main line at the junction of these two branches. By integration we find,

$$\frac{m_a}{S_a^2}\frac{dX_a}{dt} = \frac{P}{i\omega}e^{i\omega t} \tag{8}$$

the constant of integration vanishing since we are dealing with a variation in dX/dt caused by P and vanishing with P. By differentiation we obtain,

$$\frac{f_b \dfrac{dX_b}{dt}}{S_b^2} = i\omega P e^{i\omega t}. \tag{9}$$

But we know that at the junction of the branches the algebraic sum of the rate of volume displacements must be zero, or

$$\frac{dX_a}{dt} + \frac{dX_b}{dt} = \frac{dX}{dt}. \tag{10}$$

Substituting the values of dX_a/dt and dX_b/dt just found, we obtain,

$$\frac{dX}{dt} = Pe^{i\omega t}\left(\frac{1 - MC\omega^2}{iM\omega}\right), \tag{11}$$

wherein

$$M = \frac{m_a}{S_a^2} \quad \text{and} \quad \frac{1}{C} = \frac{f_b}{S_b^2}. \tag{12}$$

We will call M the *inertance*, C the *capacitance*, both defined by (12) and (7). We thus have for the impedance of the combination of the two circuits in parallel,

$$Z = \frac{iM\omega}{1 - MC\omega^2}. \tag{13}$$

Let us now assume that our impedances Z_1 and Z_2 are each composed of two such branches in parallel. The branch having mass, m_a, will vanish when $m_a = \infty$ or $M = \infty$ and the branch having stiffness, f_b, will vanish when $f_b = \infty$ or $C = 0$.

If we apply condition (5) to Z_1 and Z_2 as just determined in (13) and we have as a limiting frequency, f_1:

$$\omega^2 = \frac{1}{M_2C_2} \quad \text{or} \quad f_1 = \frac{1}{2\pi}\sqrt{\frac{1}{M_2C_2}}. \tag{14}$$

If we apply condition (6), we have:

$$\omega^2 = \frac{M_1 + 4M_2}{M_1M_2(4C_1 + C_2)} \quad \text{or} \quad f_2 = \frac{1}{2\pi}\sqrt{\frac{M_1 + 4M_2}{M_1M_2(4C_1 + C_2)}}. \tag{15}$$

In (14) and (15) the subscripts of M and C correspond to those adopted for the Z's. These frequencies f_1 and f_2 are those that limit the range in which there is no attenuation. It is to be observed that the range of no attenuation is one in which $\left(1 + \frac{1}{4}\frac{Z_1}{Z_2}\right)$ can change from $+1$ to -1.

But, from (13), Z_1/Z_2 is a continuous function of ω or $2\pi f$ and hence there is a continuous frequency range wherein there is no attenuation. A filter in which Z_1 and Z_2 each consists of an inertance and capacitance in parallel is thus possible.

C. Inertance and Capacitance in Series.

Consider each Z_1 and Z_2 to be an inertance and capacitance in series. The current must be the same throughout Z_1 or Z_2. Let P_1 be the pressure difference over the inertance, M_1, and P_2, over the capacitance, C_1. Then, from (7) and (8)

$$\frac{P_1}{i\omega M_1} = I = \frac{P_2}{\dfrac{1}{C_1 i\omega}}.$$

Hence

$$\frac{P_1 + P_2}{i\omega M_1 + \dfrac{1}{iC_1\omega}} = I$$

or

$$Z_1 = i\left(M_1\omega - \frac{1}{C_1\omega}\right). \tag{16}$$

If we now ascertain the limits of no attenuation, we have from (5),

$$f_1 = \frac{1}{2\pi}\sqrt{\frac{1}{M_1C_1}} \tag{17}$$

and from (6)

$$f_2 = \frac{1}{2\pi}\sqrt{\frac{C_2 + 4C_1}{C_1C_2(M_1 + 4M_2)}}. \tag{18}$$

Again we have the possibility of a filter.

A special and yet a common case of inertance and capacity in series is one wherein M_1 is the inertance of an orifice entering a chamber and C_1 is the capacitance of the chamber. The condition for resonance, or $Z = 0$, occurs as shown by (16) when,

$$M_1\omega = \frac{1}{C_1\omega} \qquad \text{or} \qquad f = \frac{1}{2\pi}\sqrt{\frac{1}{M_1C_1}}. \tag{19}$$

But in orifices which are short compared with their diameters we cannot use for M_1 the mass divided by the square of the area, for this expression neglects the end effects of the channel. The well-known formula for the vibration of such a system is,[1] neglecting dissipation[2]

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[1] Rayleigh, Theory of Sound, Vol. II., p. 195.

[2] Insertion of dissipation seems to lead to difficulties which are avoided by this approximation.

$$\frac{\rho}{c}\ddot{X} + \frac{\rho a^2}{V}X = Pe^{i\omega t} \tag{20}$$

from the solution of which we get,

$$\dot{X} = \frac{Pe^{i\omega t}}{i\rho\left(\dfrac{\omega}{c} - \dfrac{a^2}{V\omega}\right)}. \tag{21}$$

In these equations ρ is the density, c is the "conductivity" of the channel, a the velocity of sound and V the volume of the chamber.

It is evident that the new value of Z_1 viz.,

$$Z = i\rho\left(\frac{\omega}{c} - \frac{a^2}{V\omega}\right), \tag{22}$$

differs from (16) only by the apparent substitution of ρ/C for M_1 and $V/\rho a^2$ for C_1.

D. Inertance and Capacitance of a Tube.

In order to assist in constructing a filter, we will now discuss the nature of a column of gas, which we must use as Z_1 in our conducting line.[1]

Assume an acoustic plane simple harmonic wave passing along a tube in the direction of x. Let ξ be the displacement of a particle from its mean position; ρ the density, a the velocity of sound, and p the excess pressure over the mean.

Then

$$\rho\frac{\partial^2\xi}{\partial t^2} = -\frac{\partial p}{\partial x} \tag{23}$$

(an exact equation) and for small vibrations,[2]

$$\frac{\partial^2\xi}{\partial t^2} = a^2\frac{\partial^2\xi}{\partial x^2}. \tag{24}$$

From (23) and (24)

$$\rho a^2\frac{\partial^2\xi}{\partial x^2} = -\frac{\partial p}{\partial x}. \tag{25}$$

The integration of (25), since

$$\frac{\partial\xi}{\partial x} = 0$$

at all times when $p = 0$, gives

$$\rho a^2\frac{\partial\xi}{\partial x} = -p. \tag{26}$$

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[1] Similar discussions occur in Drysdale, Jl. of Inst. Elec. Engs., July, 1920, Vol. 58, p. 591, and Kennelly and Kurowaka, Proc. Am. Acad., Feb., 1921, Vol. 56, No. 1, p. 29.

[2] Lamb's Hydrodynamics, 1916, p. 474.

We may write (26) as follows:

$$\rho a^2 \frac{\partial \xi}{\partial x} \frac{\Delta x}{\Delta x} = -p$$

and if we represent the volume in a length Δx by ∇V, we have,

$$\rho a^2 \frac{\Delta V}{V} = -p$$

or $\rho a^2 = -E$ where E is the modulus of elasticity of volume. Since the compression is due to p and not to changes of pressure along the line, the stiffness can be considered as analogous to stiffness in the walls of the tube upon which the pressure difference p acts. Our tube possesses inertance and capacitance as we know, but the above shows that these are not the equivalent of inertance and capacitance connected either in parallel or in series. Indeed, the capacitance can be thought of as between the inside and outside of the tube instead of along the tube.

Inasmuch as we must use tubes in a practical construction it is essential that we consider whether or not a tube can be used for either Z_1, or Z_2, arranged as in the preceding theory. Consideration shows that Z_1 cannot accurately be composed of a tube, for Z_1 is wholly in the line and not between the line and the outside. Hence we must ascertain whether or not such a substitution would be a sufficient approximation. In short, can we consider a tube as having the equivalent of inertance and capacitance connected in parallel or in series, or may we consider it as having inertance only or as capacitance only?

Assume that any tube we may use will be short as compared with a wave-length. Consider the gas to move as a whole. Then the δp is due to inertance. Or consider the gas to be stationary acting as a cushion. Then δp is due to capacitance. In both cases we have neglected the change of phase along the tube. Whichever case is the better approximation will depend upon the service the tube is rendering, or, in other words, will depend upon the adjacent construction or the composition of the filter. It might appear that the tube can be approximated by lumping the capacitance. This cannot be done at the center of the section for the general theory does not permit of a side branch other than Z_2. It cannot be lumped at Z_2 as can be shown by comparison of the resulting theory with experiment. The assumption of M_1 and C_1 in series does not appear reasonable for the total pressure over the section certainly acts on M_1. We are therefore forced to the policy of using M_1 and C_1 in parallel in the line with the understanding that experiment will determine empirically whether M_1 or C_1 or both shall be used in the computations. As will subsequently be shown, experiments thus far seem to demand the introduction of C_1 in only one of the three types of filters. Thus the somewhat arbitrary manner of introducing C_1 in parallel is minimized. It is fair to say that, in this one case, the assumption seems not without a theoretical justification. It is thus observed that at the outset we are driven to an approximation which demands an empirical selection of formulæ.

III. Construction of Filters.

A. *General Limitations.*

If we are to construct an acoustic filter that will have good transmission we must avoid any changes in the nature of the medium and in the diameter of the transmitting conduit or conductor. If the filter is to have good attenuation, similar conditions would hold for the branch lines. For first experiments, then, a single medium and a transmitting line of constant cross section are chosen. These selections suggest, from the standpoint of convenience, the use of air and the use of a cylindrical tube as the boundary of the transmission line.

The only limitation to our application is that there be a series of like sections with Z_1 in the main line and Z_2 in the side branch. With no limitation placed upon the constitution of Z_1 or of Z_2, an infinite number of designs may be possible. But, as already stated, considerations lead to the selection of a cylindrical tube containing air as the transmission line. The impedance of a short section of such a line cannot be accurately expressed by an equivalent M_1 and C_1 connected either in series or parallel. We will assume M_1 and C_1 in parallel, for thereby we can make $M_1 = \infty$ or $C_1 = 0$ or remove them from consideration without obstructing the transmission of the line. But even with these limitations the number of filters is infinite, for Z_2 can be formed, theoretically, in any manner one chooses.

B. *Low Frequency, High Frequency, and Single Band Pass Filters.*

In order to determine the construction of low frequency and high frequency pass and single band filters in as simple a manner as possible, an additional provisional limitation will be made, viz., to filters in which Z_2 consists of an equivalent M_2 and C_2 connected either in series or parallel. We shall then have four quantities M_1, M_2, C_1 and C_2. If either M_1 or M_2 is absent, *i.e.*, removed from consideration, its value is infinity. Under similar conditions the value of a capacitance is zero. We have then to ascertain the possible combinations of

$$M_1 = \infty, \qquad M_2 = \infty, \qquad C_1 = 0, \qquad C_2 = 0.$$

Taken singly there are four combinations in pairs, six in triplets, four with one only, and one with none, making a total of fifteen possible combinations. If we remove those combinations which remove the *line* or the branches entirely, we have left nine designated as follows:

1. All present,
2. $M_1 = \infty$,
3. $M_2 = \infty$,
4. $C_1 = 0$,
5. $C_2 = 0$,
6. $M_1 = M_2 = \infty$,
7. $M_1 = \infty, \quad C_2 = 0$,
8. $M_2 = \infty, \quad C_1 = 0$,
9. $C_1 = 0, \quad C_2 = 0$.

By the preceding, our values of acoustical impedances are limited to the following:

In the transmission line,

$$Z_1 = \frac{iM_1\omega}{1 - M_1C_1\omega^2}. \qquad (13) \text{ bis}$$

In the branch,

$$Z_2 = \frac{iM_2\omega}{1 - M_2C_2\omega^2} \qquad (13) \text{ tris}$$

or

$$Z_2 = i\left(M_2\omega - \frac{1}{C_2\omega}\right). \qquad (16) \text{ bis}$$

If the limits of no attenuation are now ascertained by the application of equations (5) and (6) we find the values in Table I. for the nine cases, each having the possibility of Z_2 in parallel or in series.

The explanation of most of the blanks in the fourth and fifth columns is that, assuming M_2 and C_2 to be in series, our original arrangement of Z_2 providing for the same pressure in common at the termini, requires the following:

1. There must always be an M_2 at the junction point, for otherwise there could be no $\dot{X}$ and hence no use of the side branch. Hence M_2 is at the junction point and C_2 is next in the branch.

2. M_2 cannot be infinity, for if infinity, the side branch would not be used at all.

3. C_2 cannot be zero for this would prevent any value of $\dot{X}$ and therefore any use of the side branch. Thus six of the nine cases are eliminated from consideration leaving only cases 1, 2 and 4. Case 1 leads to the possibility of an imaginary frequency and introduces two values of f_2,

Table I.

Case.	Parallel.		Series.	
	f_1.	f_2.	f_1.	f_2.
1	$\frac{1}{2\pi}\sqrt{\frac{1}{M_2C_2}}$	$\frac{1}{2\pi}\sqrt{\frac{M_1+4M_2}{M_1M_2(4C_1+C_2)}}$	0	
2	$\frac{1}{2\pi}\sqrt{\frac{1}{M_2C_2}}$	$\frac{1}{2\pi}\sqrt{\frac{1}{M_2(4C_1+C_2)}}$	∞	$\frac{1}{2\pi}\sqrt{\frac{C_2+4C_1}{4M_2C_1C_2}}$
3	0	$\frac{1}{2\pi}\sqrt{\frac{4}{M_1(4C_1+C_2)}}$		
4	$\frac{1}{2\pi}\sqrt{\frac{1}{M_2C_2}}$	$\frac{1}{2\pi}\sqrt{\frac{M_1+4M_2}{M_1M_2C_2}}$	0	$\frac{1}{2\pi}\sqrt{\frac{4}{C_2(M_1+4M_2)}}$
5	∞	$\frac{1}{2\pi}\sqrt{\frac{M_1+4M_2}{4M_1M_2C_2}}$		
6	0	0		
7	∞	$\frac{1}{2\pi}\sqrt{\frac{1}{4M_2C_1}}$		
8	0	$\frac{1}{2\pi}\sqrt{\frac{4}{M_1C_2}}$		
9	∞	∞		

which are not found in experience. Knowing that the assumption of C_1 in parallel with M_1 is arbitrary, we are justified in acknowledging the incorrectness of the assumption in this case and omitting the formulæ from consideration.

These considerations lead to the development of the three following types of filters:

1. Low-frequency pass filters; case 3, parallel; case 4, series; and case 8, parallel.
2. High-frequency pass filters; case 2, series; case 5, parallel; case 7, parallel.
3. Single-band pass filters; case 1, parallel; case 2, parallel; case 4, parallel.

Conditions of construction suggest that an additional formula for the single-band filter be determined. The three cases in which we have a single-band filter as above stated, are those in which we have M_2 and C_2 in parallel. But in actual construction it is impractical to have truly a C_2 without an orifice into a volume and in this orifice we have an M_2' in series with C_2. A simple construction is thus suggested of taking *Case I* and adding an M_2' as an orifice into C_2. The impedance of the orifice and C_2 will be, according to (16)

$$Z_2' = i\left(M_2'\omega - \frac{1}{C_2\omega}\right).$$

This impedance is in parallel with the inertance M_2, the impedance of which is,

$$Z_2'' = i\omega M_2.$$

As readily follows from the definition of impedance and the fact that the sum of the two currents is the resultant branch current, the combined impedance, Z_2, is determined from the following relation,

$$\frac{1}{Z_2} = \frac{1}{iM_2\omega} + \frac{1}{i\left(M_2'\omega - \frac{1}{C_2\omega}\right)}$$

or

$$Z_2 = i\frac{M_2\omega\left(M_2'\omega - \frac{1}{C_2\omega}\right)}{M_2\omega + M_2'\omega - \frac{1}{C_2\omega}} = i\frac{M_2\omega(M_2'C_2\omega^2 - 1)}{M_2C_2\omega^2 + M_2'C_2\omega^2 - 1}. \qquad (27)$$

According to equation (13) if we make C_1 arbitrarily zero for the sake of simplicity, we have

$$Z_1 = iM_1\omega. \qquad (28)$$

If we now use the values of (27) and (28) for the conditions (5) and (6) we will have, respectively,

$$f_1 = \frac{1}{2\pi}\sqrt{\frac{1}{C_2(M_2 + M_2')}}, \qquad (29)$$

$$f_2 = \frac{1}{2\pi}\sqrt{\frac{M_1 + 4M_2}{C_2(M_1M_2 + M_1M_2' + 4M_2M_2')}}. \qquad (30)$$

C. *Computation of Inertance and Capacity.*

By comparison of (23) with (7) we see that the inertance for a straight tube, assumed to move as a whole, is,

$$M = \frac{m}{S^2} = \frac{\rho lS}{S^2} = \rho\frac{l}{S}. \qquad (31)$$

In the case of an orifice, M, as already shown, is expressed by ρ/c where c is the conductivity. The expression for c in terms of the radius, R, and length, l, of the channel is[1]

$$c = \frac{\pi R^2}{l + \frac{\pi R}{2}}. \tag{32}$$

With l large in comparison with $\pi R/2$, this reduces to S/l and $M = \rho(l/S)$ as already stated.

As shown in the discussion of (22) we should substitute $V/\rho a^2$ for C_1. Therefore our equations for substitution are:

$$M = \frac{\rho}{c} = \frac{\rho\left(l + \frac{\pi R}{2}\right)}{\pi R^2} \tag{33}$$

and

$$C = \frac{V}{\rho a^2}. \tag{34}$$

D. *Form of the Filters.*

(*a*) *Low-Frequency Pass Filter.*—In a preceding section we found at least three formulæ for a low-frequency pass filter. They are as follows:

$$f_1 = 0, \qquad f_2 = \frac{1}{\pi}\sqrt{\frac{1}{M_1(4C_1 + C_2)}} = \frac{1}{\pi}\sqrt{\frac{1}{M_1C_2 + 4M_1C_1}}, \tag{A}$$

requiring that C_2 be the only portion of the branch;

$$f_1 = 0, \qquad f_2 = \frac{1}{\pi}\sqrt{\frac{1}{C_2(M_1 + 4M_2)}} = \frac{1}{\pi}\sqrt{\frac{1}{M_1C_2 + 4M_2C_2}}, \tag{B}$$

requiring that M_2 and C_2 be connected in series and that C_1 be zero;

$$f_1 = 0, \qquad f_2 = \frac{1}{\pi}\sqrt{\frac{1}{M_1C_2}}, \tag{C}$$

requiring that C_2 be the only portion of the branch and that C_1 be zero.

All these formulas are dimensionally correct and there is no conclusive evidence showing that one is superior to another save by actual experiment. Attention may be called, however, to the difficulty of constructing a C_2 without an M_2 in series. With C_2 only the most favorable cross-section of construction would be similar to Fig. 3. But there would be an M_2 and the justification for neglecting it would be raised.

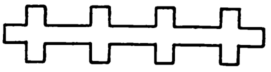

Fig. 3.

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[1] Rayleigh, Theory of Sound, Vol. II., p. 181.

If the construction is made as in Fig. 4, the M_2 is better defined and can be determined from equation (33). These considerations point to the use of (*B*).

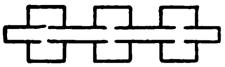

Fig 4.

(*b*) *High-Frequency Pass Filter.* — We previously found three simple cases of a high-frequency pass filter. The formulæ are as follows:

$$f_1 = \infty, \qquad f_2 = \frac{1}{2\pi}\sqrt{\frac{C_2 + 4C_1}{4M_2C_1C_2}} = \frac{1}{2\pi} = \sqrt{\frac{1}{4M_2C_1} + \frac{1}{MC_{22}}} \tag{D}$$

requiring that $M_1 = \infty$;

$$f_1 = \infty, \qquad f_2 = \frac{1}{2\pi}\sqrt{\frac{M_1 + 4M_2}{4M_1M_2C_1}} = \frac{1}{2\pi}\sqrt{\frac{1}{4M_2C_1} + \frac{1}{M_1C_2}} \tag{E}$$

requiring that $C_2 = 0$;

$$f_1 = \infty, \qquad f_2 = \frac{1}{2\pi}\sqrt{\frac{1}{4M_2C_1}}, \tag{F}$$

requiring that $M_1 = \infty$ and $C_2 = 0$. Formula (*E*) and (*F*) indicate that it might be possible to construct such a filter with a straight tube and side branches consisting of M_2 only, or consisting of orifices. This plan has been followed in the filters herein described.

(*c*) *Single-Band Filter.*—We previously found four simple single-band filters. The formulæ are as follows:

$$f_1 = \frac{1}{2\pi}\sqrt{\frac{1}{M_2C_2}}, \qquad f_2 = \frac{1}{2\pi}\sqrt{\frac{M_1 + 4M_2}{M_1M_2(4C_1 + C_2)}}$$

$$= \frac{1}{2\pi}\sqrt{\frac{1}{M_2C_2}\left[\frac{1 + 4\frac{M_2}{M_1}}{1 + 4\frac{C_1}{C_2}}\right]}, \tag{H}$$

requiring that all of the four elements remain in consideration;

$$f_1 = \frac{1}{2\pi}\sqrt{\frac{1}{M_2C_2}}, \qquad f_2 = \frac{1}{2\pi}\sqrt{\frac{1}{M_2(4C_1 + C_2)}}$$

$$= \frac{1}{2\pi}\sqrt{\frac{1}{M_2C_2}\left[\frac{1}{1 + 4\frac{C_1}{C_2}}\right]}, \tag{I}$$

requiring that $M_1 = \infty$;

$$f_1 = \frac{1}{2\pi}\sqrt{\frac{1}{M_2C_2}}, \qquad f_2 = \frac{1}{2\pi}\sqrt{\frac{M_1 + 4M_2}{4M_1M_2C_2}}$$

$$= \frac{1}{2\pi}\sqrt{\frac{1}{M_2C_2}\left[\frac{1}{4} + \frac{4M_2}{M_1}\right]}, \tag{J}$$

requiring that $C_1 = 0$. The fourth pair of values requiring that $C_1 = 0$ is found in equations (29) and (30) or

$$f_1 = \frac{1}{2\pi}\sqrt{\frac{1}{M_2C_2}\left[\frac{1}{1+\dfrac{M_2'}{M_2}}\right]}, \quad f_2 = \frac{1}{2\pi}\sqrt{\frac{1}{M_2C_2}\left[\frac{1+4\dfrac{M_2}{M_1}}{1+\dfrac{M_2'}{M_2}+\dfrac{4M_2'}{M_1}}\right]}. \qquad (K)$$

E. Empirical Character of Formulæ.

We are prevented from securing accurate formulæ by the following circumstances:

1. Our dimensions cannot be vanishingly small as compared to a wave-length and therefore appreciable phase differences occur in any section or branch.

2. We cannot get an accurate expression for the impedance of a short tube because our theory assumes that this impedance is strictly in the line, whereas a tube has distributed capacitance virtually between itself and the undisturbed surrounding medium.

3. One hypothesis upon which the theory is based assumes that the junction points are really points, *i.e.*, there can be no accumulation there.

In respect to these circumstances stated, it is fair to say that the accuracy of the approximations cannot be estimated save by experiment. It is allowable, therefore, to take the position that we are to seek, in the case of each construction, that pair of formulæ which seems best to agree with experiment. In other words, the formulæ are somewhat empirical, though their manner of derivation gives a reason for their forms. This attitude of empiricism does not, then, hide the nature of the phenomena but rather decides as to the best approximation.

IV. Comparison of Theory and Experiment.

A. Measurement of Transmission.

An apparatus, Fig. 5, similar to that used by Drs. Gray and Roebuck, but not described in print, gave sufficiently accurate measurements of the transmission of the filters. T_1 and T_2 are similar telephone receivrse, V is a valve connecting a pair of stethoscope binaurals to either T_2 or

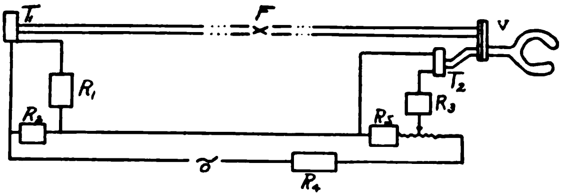

Fig. 5.

the tube which connects to the filter F and T_1, the resistance boxes are marked by the R's, and the source of sinusoidal currents is an oscillator loaned by the Western Electric Company. The circuits of the latter consist of an oscillating circuit, an amplifier, an electrical low-frequency pass filter of two sections, a resistance R_4, and inductances and capacities by means of which it was possible to get fairly pure tones from 90 to 1,500 vibrations and tones up to 5,000 without the use of a filter. R_2 was small in comparison with R_1 and the latter about ten times the impedance of T_1 for a frequency of 1,000 cycles. R_5 was never greater than one tenth the impedance of T_2 and R_3. The brass tubing on either side of F was .557 cm. in internal diameter and 2.5 meters long. The method pursued was to adjust the values of the R's so that, without the acoustic filter present, the values of R_5 required to produce the same intensity at the stethoscope with either acoustic connection, were not in excess of the limit above stated. Each filter had its conducting tube of approximately the same diameter as the tubes from F_1 to T_1 and V. Settings of R_5 were recorded for the various frequencies with and without F, in the latter case a tube of the same length and internal diameter being substituted for F. The transmitted intensities were assumed proportional to the square of R_5. Thus the percentage transmission of F at a certain frequency would be the ratio between the squares of R_5 with F and with its substitute tube. Obviously, the tubes in the apparatus have resonance and this will greatly reduce the accuracy of the transmission values. For frequencies lower than 2,000, pieces of hair felt were inserted every 15 cm. or so to increase the viscosity and reduce resonance. Improved readings were then obtained. The curves herewith presented must be examined with the understanding that resonance does exist. Since our immediate object was merely to get an estimate of the filtering action rather than an accurate measure of transmission, no effort at further refinement was considered. Experiments showed that even with the felt present, variations of 10 per cent. to 20 per cent. apparent transmission with frequency might occur.

B. Low-Frequency Pass Filters.

The general construction of the low-frequency pass filters and the experimental transmission curve is shown in Fig. 6. The accompanying Table II. gives the dimensions, the computations and certain experimental facts concerning a number of low-frequency filters. In this Table l, r, and V refer to the length of section, internal radius and volume respectively. The subscript 1 refers to the conducting line or tube and the subscript 2 to the branches or in the case of the form here used, to the surrounding tube. The value f_m is the value of the frequency at which the transmission is 50 per cent. of the "unattenuated" transmission of the filter. Inasmuch as the beginning of attenuation cannot be sharp, this mean value is perhaps the fairest selection of an experimental value. The computations indicated by the letters, A, B, and C were made according to the formulæ so marked in the preceding theory. These formulæ when expressed in terms of the dimensions become, after

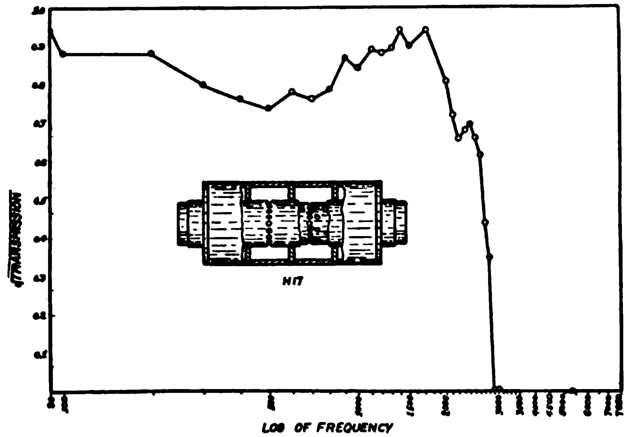

Fig. 6.

substitution in accord with (31), (33) and (34), respectively, (A'), (B') and (C') as follows:

$$f_1 = 0, \qquad f_2 = \frac{a}{\pi}\sqrt{\frac{S_1}{l_1 V_2}\left[\frac{1}{1 + 4\dfrac{l_1 S_1}{V_2}}\right]}, \tag{A'}$$

$$f_1 = 0, \qquad f_2 = \frac{a}{\pi}\sqrt{\frac{S_1}{l_1 V_2}\left[\frac{1}{1 + 4\dfrac{S_1}{c l_1}}\right]}, \tag{B'}$$

$$f_1 = 0, \qquad f_2 = \frac{a}{\pi}\sqrt{\frac{S_1}{l_1 V_2}}\,. \tag{C'}$$

It is evident that the formula (B') is to be preferred since it gives approximately the experimental values of f_m and also explains satisfactorily the variation of the frequency limit of attenuation with the conductivity of the orifices leading from the transmission conduit to the volume in the branch.

Attention should be directed to several other facts shown in the table. The percentage transmission in the "unattenuated" region given in column "T," seems to depend upon the ratio between r_2 and r_1, the

TABLE II.

No.	No. of Sections.	l_1 cm.	r_1 cm.	r_2 cm.	V_{2_3} cm.	f_m d.v.	$f_2(A')$ d.v.	$f_2(B')$ d.v.	$f_2(C')$ d.v.	No. of Apertures.	T %.	*Faf*	
												f	%.
2	3	2.66	.243	1.71	21.6	450	595	462	624	2	.20	5,250	708
3	5	5.0	.243	1.71	43.1	230	308	291	321	4	.36	3,100	933
13	4	4.0	1.42	2.57	44.4	920	1,140	880	2,075	6	.80	3,300	106
15	4	1.67	.75	1.42	5.94	2,200	2,670	2,710	4,620	16	.80	5,150	106
15	4	1.67	.75	1.42	5.94	1,700	2,670	2,120	4,620	8		2,900	38
16	4	1.67	.75	1.15	2.62	3,200	2,965	4,085	6,960	16		6,200	55
16	4	1.67	.75	1.15	2.62	2,500	2,965	3,200	6,960	8		4,000	29
17	4	1.67	.75	1.30	4.36	2,700	2,800	3,175	5,400	16	.65	5,200	66
17	4	1.67	.75	1.30	4.36	2,200	2,800	2,480	5,400	8		3,000	25
R 1	3	1.58	1.19	1.82	7.1	2,700	3,080	2,840	6,885	8	.90	3,500	9.4
R 2	4	1.58	1.19	1.82	7.1	2,750	3,080	2,840	6,885	8	.72	4,000	25
R 3	4	1.32	1.19	1.82	5.87	3,350	3,700	3,170	8,300	8	.72	4,750	18.7
R 4	4	1.45	1.19	1.82	6.48	3,025	3,370	3,010	7,520	8	.90	4,600	65
R 5	6	2.58	1.19	1.82	11.82	2,000	1,890	2,095	4,180	8	.90	3,000	25
R 6	6	1.58	1.19	1.82	7.1	2,700	3,080	2,700	6,885	4	.90	4,750	44
R 6	6	1.58	1.19	1.82	7.1	2,075	3,080	2,100	6,885	4	.72	3,100	24

number of sections constant, the greater the ratio the less the transmission. In the last two columns labeled "*Faf*," the one under "*f*" refers to the first audible frequency above the cut-off, and under "%" the ratio between the range of inaudibility and the actual cut-off. Here we note that while filters in which r_2/r_1 is large have inferior transmission, yet they have a surprisingly great range of frequencies above the cut-off where the filter operates successfully. In filters 2 and 3 this range is at least over ten times the cut-off frequency. As the ratio of r_2/r_1 becomes smaller, this cut-off range decreases but the transmission in the "unattenuated" region improves. It is impossible to select, without specifications and trial, the most successful design for a given frequency cut-off, for success depends upon both the range of cut-off and upon the percentage of transmission in the unattenuated region desired. The remarkable feature is that the high attenuation in the region above the theoretical lower limit, f_2, is ever as great as ten times this limit. In fact, in the case of No. 2, that frequency having a wave-length of approximately the length of a section is highly attenuated. The performance is better than one would hope. Attention is directed to *R* 1, a tube about 6 cm. long and 2.4 cm. in diameter yet capable of having an attenuation producing inaudible transmission for a considerable range above the cut-off. Such a performance is a surprise to one accustomed to the difficulty in preventing the passage of sound through holes and channels.

C. *High-Frequency Pass Filters.*

We previously have mentioned three possible simple cases of a high-frequency pass filter but two of these seemed to consist merely of a straight tube with side branches each having an M_2 or orifices, only. The cross-section of such a filter and its transmission is shown in Fig. 7.

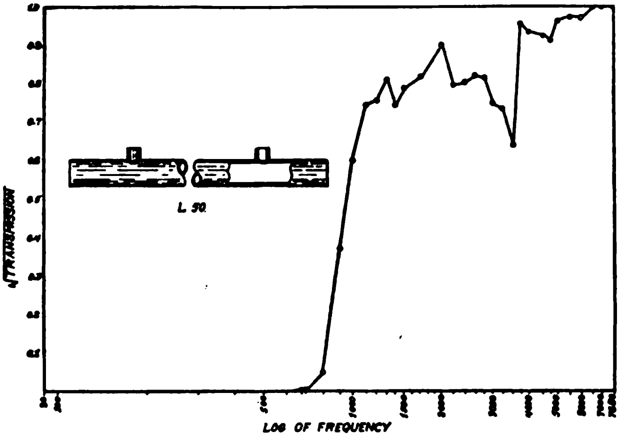

Fig. 7.

If we substitute in the formulæ, (E) and (F) in accord with (33) and (34), we obtain the following:

$$f_1 = \infty, \qquad f_2 = \frac{a}{2\pi}\sqrt{\frac{c}{4V_1}}\left(1 + \frac{4S_1}{l_1 c}\right), \tag{E'}$$

$$f_1 = \infty, \qquad f_2 = \frac{a}{2\pi}\sqrt{\frac{c}{4V_1}}, \tag{F'}$$

wherein c is the conductivity of the orifice as defined in (32).

Data of several filters of differing dimensions are given in Table III. The last column found in Table II. is here omitted because these filters gave transmission up to the highest frequency tried—5,000–7,000 d.v. The experimental results are therefore strictly in accord with the limits of attenuation set by the theory from f_2 to zero. A reason is doubtless that the less the frequency the more nearly the experimental conditions meet those assumed in the theory.

The general conclusion is that the formula (E') is very satisfactory. It is to be noted that in (E) we have used C_1. This is the only case of the three where experiment has indicated that C_1 should be used. As stated in the discussion of the theory, the assumption of C_1 in parallel with M_1 is arbitrary. A justification may now be seen in the following fact. The branch lines, M_2, are short. Thus there is a much greater

TABLE III.

No.	No. of Sections.	l_1 cm.	r_1 cm.	l_2 cm.	r_2 cm.	c.	f_m.	$f_2(E')$.	$f_2(F')$.	T.
15 II....	8	2.5	.243	0.5	.115	.061	2,300	2,400	988	.75
19......	4	5.0	.243	0.5	.115	.061	1,500	1,300	699	.60
22......	8	2.5	.243	0.5	.152	.099	2,200	2,520	1,262	.50
1,2,3,4..	8	4.0	.483	1.22	.278	.146	1,500	1,490	610	.75
50......	12	5.0	.483	0.5	.139	.0845	920	1,170	415	.85
50......	6	10.0	.483	0.5	.139	.0845	810	620	293	.90
50......	4	15.0	.483	0.5	.139	.0845	525	436	240	.90
50......	3	20.0	.483	0.5	.139	.0845	450	344	207	.90

pressure gradient in M_2 than in the conduit or conducting line itself. The particle velocity in M_2 is therefore much greater than in the conduit. If the particle velocity in the line were actually at rest, the conduit would serve as a capacitance for M_2. Thus, the existence of an effective capacitance is not surprising.

Attention should be called to the fact that experiment showed that as M_2 was made longer or very narrow, introducing viscosity, the cut-off became less sharp.

D. *Single-Band Filters.*

We have already presented four pairs of formulæ for single-band filters. If we now have a filter of the construction shown in Fig. 8 and denote by l_2, S_2 the length and area of the side tube and by c the conductivity of the holes from the side branch into the chamber V_2, these four formulæ

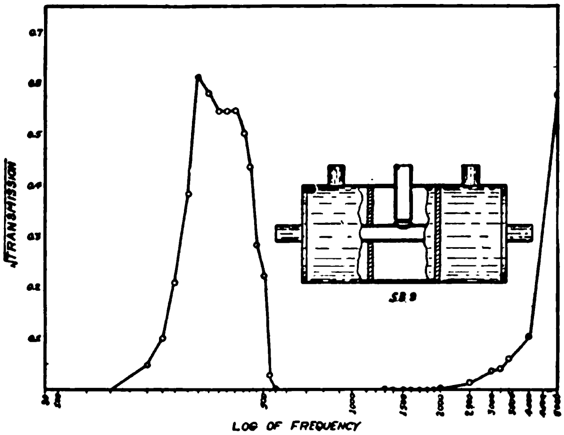

Fig. 8.

may be written after substitution according to (33) and (34) as follows:

$$f_1 = \frac{a}{2\pi}\sqrt{\frac{S_2}{{}_2lV_2}}, \qquad f_2 = \frac{a}{2\pi}\sqrt{\frac{S_2}{l_2V_2}\left[\frac{1 + 4\frac{l_2S_1}{l_1S_2}}{1 + 4\frac{l_1S_1}{V_2}}\right]}, \qquad (H')$$

$$f_1 = \frac{a}{2\pi}\sqrt{\frac{S_2}{l_2V_2}}, \qquad f_2 = \frac{a}{2\pi}\sqrt{\frac{S_2}{l_2V_2}\left[\frac{1}{1 + 4\frac{l_1S_1}{V_2}}\right]}, \qquad (I')$$

$$f_1 = \frac{a}{2\pi}\sqrt{\frac{S_2}{l_2V_2}}, \qquad f_2 = \frac{a}{2\pi}\sqrt{\frac{S_2}{l_2V_2}\left(1 + 4\frac{l_2S_1}{l_1S_2}\right)}, \qquad (J')$$

$$f_1 = \frac{a}{2\pi}\sqrt{\frac{cS_2}{V_2(l_2c + S_2)}}, \qquad f_2 = \frac{a}{2\pi}\sqrt{\frac{S_2}{l_2V_2}\left[\frac{1 + 4\frac{l_2S_1}{l_1S_2}}{1 + \frac{S_2}{l_2c} + \frac{4S_1}{cl_1}}\right]}. \qquad (K')$$

Fig. 8 also shows the transmission curve of one of the filters, *SB*9, with which the range of highly attenuated frequencies above f_2 is relatively small. The two-column "*Faf*" in Table IV. is similar to that in Table II. The reasons for the lack of attenuation in these high frequencies are doubtless the same as in the case of the low-frequency pass filters described in a previous section. For, as will be observed, the single-band filter may be looked upon as a combination of the two other types. The experimental results show the (K') formulæ to be the most satisfactory.

V. Discussion and Conclusions.

The high attenuation secured with but few sections was not anticipated. General experience in acoustics increases the remarkableness of the action of the filters. The agreement with the theory is, in view of the assumptions made, fairly satisfactory for it is possible to construct filters that meet specifications.

The physical action considered herein is clearly not dissipation but interference. With a source transmitting energy through a filter, the action of the latter is to prevent the emission of energy from the source in these frequencies for which there is attenuation. There is dissipation, or at least a decrease in transmission in the filters, extending over the unattenuated region and this seems to be the greater, in the case of the low-frequency-pass filter, the greater the ratio of r_2 and r_1.

The extent of the usefulness of the filter will be determined by experience. Its simplicity and cheapness of construction make it a serviceable

TABLE IV.

No.	No. of Sections.	l_1 cm.	r_1 cm.	l_2 cm.	r_2 cm.	V_2 cm.^{3}	c	Observed.		Computed.						T %.	Faf	
								f_1	f_2	$f_1(H'I'J')$	$f_2(H')$	$f_2(I')$	$f_2(J')$	$f_1(K')$	$f_2(K')$			%.
1	3	5.0	.243	2.33	.243	42.7	0.69	190	260	236	380	227	400	224	346	.12	3,000	900
2	3	2.66	.243	2.33	.243	21.19	0.69	275	375	304	680	322	710	318	575	.26	3,000	500
3	3	5.0	.243	2.20	.243	28.02	0.69	270	370	300	468	282	499	283	430	.23	2,200	389
4	3	2.66	.243	1.70	.243	14.81	0.69	430	520	470	830	441	882	436	707	.28	3,125	400
5	3	5.0	.243	3.35	.243	28.02	0.69	190	270	242	439	228	466	234	410	.28	2,100	425
6	3	2.66	.243	2.80	.243	14.81	0.69	350	500	366	782	344	835	349	680	.29	3,000	400
7	3	1.17	.243	1.20	.243	5.74	0.69	700	1,300	836	1,875	835	2,030	810	1,380	.54	3,200	129
9	3	2.66	.243	2.40	.243	22.7	.455	285	475	319	648	306	685	295	506	.37	1,300	106
10	4	1.77	1.12	0.5	.278	14.4	.58	600	1,250	1,407	2,255	960	3,590	1,080	1,530	.56	1,800	33

device. In the laboratory it can be used in the elimination of undesirable components in a sound wave, and for certain types of sound analysis. In the latter case its advantage over a resonating device is its selection of a band of adjustable width. Its possible fields of usefulness in practical instruments may be merely mentioned. In the rendition of records on the phonograph and in the wireless telephone many undesirable frequencies can be removed. In wireless telegraphy an acoustic filter makes possible the simultaneous reception of an indefinite number of messages with the same antenna. In connection with a megaphone on a loud-speaking device, the filter has also an application. The introduction of this new filtering phenomenon may in time affect the design of musical instruments. Although the future use of the acoustic filter cannot be foreseen, there is one fundamental fact to be recognized, namely, that an aerial wave is used in audition and that a modification of this wave by a strictly acoustical method wherein the air is the medium, gives an opportunity for the energy to flow directly from the filter to the ear without any transformation which would introduce undesirable modifications. These acoustic filters have a great acoustic interest and the investigation of them, both theoretical and experimental, is being continued.

Physical Laboratory,
State University of Iowa.

A STUDY OF THE EXCITING POWER FOR FLUORESCENCE OF THE DIFFERENT PARTS OF THE ULTRAVIOLET SPECTRUM.

BY LELAND JAYNES BOARDMAN.

SYNOPSIS.

Intensity of Fluorescence as a Function of Wave-length of Exciting Light, 0.55 to 0.2 μ.—The purpose of the experiment was to determine what wave-lengths are effective in excitation and what relations exist between these wave-lengths and the corresponding absorption and fluorescence spectra. Light from a source giving a continuous spectrum was dispersed by means of a quartz spectrograph and allowed to fall on the substance to be studied which was spread on a flat surface. Then the parts of the spectrum which excited fluorescence were observed or photographed by means of the fluorescent light. *A preliminary study of seventy substances* showed that all the oxides (20) and simple chlorides (8) tested were not excited, a few substances (7) including zinc silicate, zinc sulphate and cadmium phosphate fluoresced faintly, a few responded well (anthracene, eosin, fluorescein, phenolphthalein, calcium tungstate, and phosphorescent willemite), while the uranyl compounds (20) fluoresced strongly. For the last group the effective spectrum extended from 0.55 to 0.35 μ only, while for the others it extended continuously to 0.2 μ except in the case of four substances for which light from 0.35 to 0.325 was ineffective. *Excitation band spectrum for twelve uranyl compounds* was determined by measuring the density of the plates as a function of the wave-length by means of a sensitive photoelectric spectrophotometer. Some curves are reproduced and the wave-numbers corresponding to from 35 to 105 maxima for each compound are given. *Comparison with absorption spectra* shows close agreement, an absorption band corresponding to an excitation band in every case. This relation had previously been found by Howe to hold for phosphorescent sulphides.

Absorption Spectrum of Twelve Uranyl Compounds, from 0.55 to 0.32 μ.—Because of the correspondence noted above the excitation bands may be taken to be absorption bands and thus the known absorption spectrum be considerably extended toward both the red and ultraviolet. Comparison of these bands with the fluorescence spectrum indicates clearly many new reversing regions where the fluorescent light obscures the absorbing effect. These are listed.

INTRODUCTION.

THE purpose of this investigation is to study the behavior of different portions of the ultraviolet spectrum as regards the ability of exciting fluorescence. The major part of previous work in fluorescence has been confined to a study of the fluorescence and absorption spectra of various materials and the relations between the two. This enables one to describe the phenomena, or state what happens as the result of the mechanism producing fluorescence. It also throws some light on the nature of the mechanism itself.

It seemed probable that something could also be learned about this mechanism by studying the means by which it is set in operation: in other words by studying the conditions and means by which fluorescence is excited. As a part of this problem it is of interest to determine what wave-lengths are effective in excitation and what relations exist between the excitation, absorption, and the fluorescence spectra. Almost the only work that has been done along this line is that of Stokes,[1] and, for a certain group of materials, the work of Lenard.[2]

The method of the present investigation is similar to that used by Stokes. Quartz was however used in place of glass, and better sources of ultraviolet light were employed. Fig. 1 shows the arrangement of the apparatus. Light from the source *S* passed through a spectrograph, and then fell upon the fluorescent substance mounted in the plane of the plate-holder of the spectrograph at *A*.

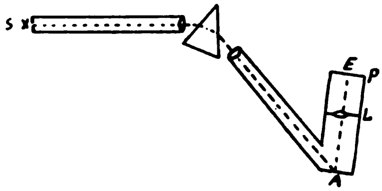

Fig. 1.

With the room darkened the fluorescence was studied for color and relative intensity by the eye at *E*. For more accurate study a photograph was taken by means of a camera lens *L* and a plate at *P*. In this way the exciting power of any region of the ultraviolet light was easily determined, since the dispersed light fell immediately upon the specimen spread out to intercept the entire beam of light.

It was necessary to use a light source which gives a continuous ultraviolet spectrum as free as possible from lines or bands. An electric spark under water was quite satisfactory for a large range of the ultraviolet spectrum. Other sources of light could be used to better advantage however in the visible and near ultraviolet region, since it was very difficult to maintain a spark in water for a sufficiently long time to give a proper exposure for the regions of weak fluorescence. Some photographs were however obtained by long excitation by the spark. By the method of producing the under-water spark used in this work, which is described in another paper soon to be published, it was possible to maintain a vigorous spark discharge 8 mm. in length for half an hour in distilled water, by means of a Tesla coil operated by a transformer of one kilowatt capacity.

It was found that a 400 c.p. nitrogen-filled glass-bulb Mazda lamp gave sufficient intensity in the near ultraviolet, and this was used when possible because of its greater convenience. For somewhat shorter wavelengths a similar lamp with a quartz bulb was used.

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[1] Stokes, Phil. Trans., p. 463, 1852.

[2] Lenard, P. Ueber Lichtemission und deren Erregung. Annalen der Physik, 31, p. 641, 1910.

Two spectrographs were used: the Fuess type, which gives a spectrum about 5 cm. long, range 580 $m\mu$ to 200 $m\mu$, and a Hilger instrument which gives five regions (5 settings) of the spectrum with a total length of about 30 cm., range 800 $m\mu$ to 205 $m\mu$. This spectrograph, which proved to be excellent for the purpose, is constructed so that five adjustments of its parts can be made for each of the five ranges or parts of the spectrum. The ranges are: 800 to 400 $m\mu$, 400 to 305, 305 to 255, 255 to 225 and 225 to 205. The five adjustments are: position of collimating lens, angle at which the prism is set, the angular position of the arm carrying the plate-holder, the position of the objective lens, and the angle which the plane of the plate-holder makes with the axis of the plate-holder arm. The data furnished by the makers for the various adjustments were corrected for this particular instrument and plotted in such a way as to show the relation between each variable and the corresponding range. It was found that practically linear relations existed, so that it was possible to set for any intermediate range desired by merely interpolating between the given settings. A split quartz prism was used.

PRELIMINARY STUDY.

A visual study of a great number of substances was made in order to find out what parts of the ultraviolet spectrum were most capable of exciting fluorescence, and also what substances respond best to such excitation, and were therefore suitable for further study. The Fuess spectrograph was mounted in such a way as to make the plane of the plate-holder horizontal. The substance was spread out on a piece of glass or stiff paper and held in the plane of the plate-holder. The following substances were examined in this way, a record being made in each case of the amount and position of the fluorescence excited by the ultraviolet *only* (since the dispersion in this region was good whereas the visible part was very narrow). The uranyl compounds exhibited the strongest fluorescence. They are given in the order of relative intensity, the first being the brightest.[1]

Rubidium uranyl nitrate,
Rubidium uranyl sulphate,
Potassium uranyl sulphate,
Potassium uranyl nitrate,
Potassium uranyl chloride,
Lead uranyl acetate,
Ammonium uranyl nitrate,
Mercury uranyl acetate,
Calcium uranyl acetate,
Strontium uranyl acetate,

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[1] The following uranyl compounds were found to fluoresce most strongly under x-ray excitation: Rubidium uranyl nitrate, rubidium uranyl sulphate, cesium uranyl chloride and lithium uranyl acetate.

Ammonium potassium uranyl chloride,
Cesium uranyl chloride,
Lithium uranyl acetate,
Cadmium uranyl acetate,
Barium uranyl acetate,
Uranyl acetate,
Sodium copper uranyl acetate,
Silver uranyl acetate,
Uranyl tellurate,
Thanous uranyl sulphate.

Other substances responding well to ultraviolet excitation were:

Anthracene, Phenolphthalein,	variable but continuous excitation between 550 and 200 mμ.
Calcium tungstate, Phosphorescent willemite, Fluorescein, Eosin,	excitation between 550 and 350 mμ and between 325 and 225 mμ approximately. Last two substances dissolved in water or alcohol.

The following substances fluoresced faintly by ultraviolet excitation:

CaC_2O_4,
Zinc silicate,
Zinc sulphate,
Cadmium phosphate,
Phosphorescent calcite.
Sodium uranyl cobalt acetate.
Sodium molydate.

The following substances were practically unaffected by ultraviolet excitation:

Barium chloride,
Barium sulphate,
Berylium chloride,
Calcium fluospar,
Calcium sulphate,
Cadmium iodide,
Cesium chloride,
Didymium chloride,
Lead chloride,
Naphthol yellow,
Potassium iodide,
Rubidium chloride,
Sodium chloride,
Sodium silicate,
Telluric acid,
Thallun sulphate,
Tungstic acid,
Vanadium chloride,

and the oxides:

Al_2O_3, CaO, Cr_2O_3, PbO, NiO, SiO, UO_3,
BaO, CeO_2, CuO, MgO, Ni_2O_2, SnO_2, ZnO.
Bi_2O_3 CeO, FeO, MnO, Sb_2O_3, TeO_2,

Three general types of excitation were observed. First, a broad continuous region of excitation, somewhat variable in intensity and becoming gradually weaker further out in the ultraviolet. Second, strong in the violet and near ultraviolet to about 350 mμ where the fluorescence seems to dissappear over about 25 mμ then to reappear over a region about 100 mμ long with a maximum at about 275 mμ. Third, strong in the violet and near ultraviolet to about 350 mμ where the intensity drops very rapidly to practically zero in some cases or to a relatively small value beyond which point the intensity gradually fades away. No fluorescence was observed beyond 200 mμ. Anthracene is a good example of the first type, calcium tungstate and fluorescein are good examples of the second type, and the uranyl compounds illustrate the third type.

Photographs were obtained of the fluorescent light emitted from nearly all of the substances listed above which show any appreciable effect. The means of mounting the material is described in the following paragraph. It was very difficult to secure good photographs in some cases, particularly with the liquid solutions of fluorescein and eosin. The Fuess spectrograph was used and a camera lens of 7 inches focal length. Exposures ranging from one minute to thirty minutes were necessary.

METHOD OF MOUNTING THE FLUORESCENT SUBSTANCE.

It was necessary to have the fluorescent material offer a smooth surface to the exciting light in order to obtain a good record on the photographic plate, to which end the following simple method was used. A strip of varnish or glue about two centimeters wide was made across the whole width of the plate, and the powdered substance was sprinkled over this with sufficient depth to cover it completely. Another glass plate was then used to press upon on rub this surface till it was made as smooth as possible. Care was taken not to leave any part of the surface in a matte white condition due to rubbing, as such a part may appear on the photograph to be different from its surroundings. In case of some of the uranyl salts the natural crystals are very hard to reduce to fine enough granulations to make a smooth surface possible in this way. Some of the photographs show this. In case of liquids or solutions a strip of quartz was used, and it was mounted in such a way as to cover the portion of liquid to be exposed.

FURTHER STUDY OF THE URANYL COMPOUNDS.

It was mentioned above that the uranyl compounds were excited to fluorescence by wave-lengths of light lying between 550 $m\mu$ and 350 $m\mu$. (Excitation by shorter wave-lengths than this was very feeble, too faint indeed to be photographed.) In the most intense part of the excitation, as photographed by the Fuess spectrograph, there appears to be a short region in which the excitation is variable, giving what might be called bands, and this region is the same as that in which absorption bands for these same materials are found. Now fluorescence is undoubtedly due primarily to absorption, though it cannot be assumed that greater absorption will produce proportionately greater fluorescence. It seems reasonable nevertheless to expect that there may be some variation in the excitation where there is variable absorption. If it is true that the variation in the intensity of the fluorescence is due to the changing absorption of the dispersed exciting light, this method might well be used in detecting and studying the absorption of materials, for if light of a particular wave-length is absorbed and this excites fluorescence which emanates from the same, or neighboring, spot, it would be very easy to observe this photographically in case there is good dispersion of the exciting light. The work that follows is an attempt first to test the validity of the assumption by seeing if fluorescence bands *do* occur where absorption bands are known to exist, and, if the results confirm the assumption, to locate the position of as many absorption bands as this method is capable of giving, and thereby to test the laws which have been found to govern the arrangement of the bands previously observed. The uranyl salts are particularly good for this work because they give many narrow bands, both in the fluorescence region of the spectrum and in the absorption region.

THE FOLLOWING ARE THE COMPOUNDS TESTED:

1. Barium uranyl acetate,
2. Lithium uranyl acetate,
3. Mercury uranyl acetate,
4. Strontium uranyl acetate,
5. Uranyl acetate,
6. Sodium copper uranyl acetate,
7. Cesium uranyl chloride,
8. Potassium uranyl chloride,
9. Potassium uranyl nitrate,
10. Rubidium uranyl nitrate,
11. Cesium uranyl sulphate,
12. Rubidium uranyl sulphate.

Nichols and Howes[1] in their recent treatise entitled "Fluorescence of the Uranyl Salts" give a summary of results showing the distribution and character of the fluorescence spectrum and the absorption spectrum of many uranyl compounds. It is shown that the spectrum of the fluorescent light consists of bands which naturally form eight groups of five members each, approximately, ranging from 640 $m\mu$ to 490 $m\mu$, or thereabouts. The absorption spectrum consists also of bands having about the same arrangement, but ranging from 490 $m\mu$ to 380 $m\mu$, apparently a continuation of the fluorescence spectrum. The frequency intervals (reciprocal wave-length intervals) between homologous bands of each group are practically the same throughout the spectrum of either, the interval being about 86 in the fluorescence spectrum and about 70 in the absorption spectrum. The last member of the fluorescence series is usually coincident with or at a distance from the first member of the absorption series of the homologous band of 86 or 70 frequency units. Considering all of the series of the various homologous bands there is an overlapping of the fluorescence and absorption spectra of about three groups, called the "reversing region" because here there are coincidences of fluorescence and absorption bands.

In this work a glass-bulb nitrogen-filled tungsten lamp, running at 6 amperes, was used as a source of ultraviolet light. A quartz mercury lamp was used[1] for calibration purposes, the calibration spectrum being photographed alongside of the other spectrum by exposing an adjacent portion of the slit of the spectrograph, both exposures taking place at the same time.

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[1] Nichols and Howes, Carnegie Inst. Wash. Pub., No. 298, 1919.

The intensity of blackening of the plates was measured by means of a device set up by J. O. Perrine in connection with his work[2] on "A Spectrographic Study of Ultraviolet Fluorescence Excited by X-rays." The apparatus makes use of a photo-electric cell, *C* in Fig. 2, and a sensitive galvanometer *G*. The cell, which was selected after trial of several types, was made by Kunz.[3] A Leeds and Northrup type *C* galvanometer was used about 6 meters from the scale near the comparator and cell. The comparator carried the photographic plate *P* just under a slit 2 mm. by .25 mm., through which a strong beam of light from an incandescent lamp *L* was passed. The lamp had one filament carrying a current of about 6 amperes from a storage battery. The current could be adjusted to meet the needs of the plate. *E* is a constant potential dry battery of about 80 volts. Further description of the apparatus is given in the paper just cited.

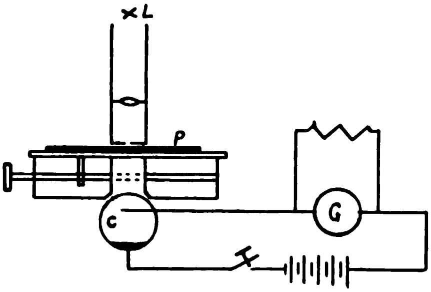

Fig. 2.

Much of the success of the present work is due to this apparatus. The instrument, which is highly sensitive to any variation in the density of the photographic image, has many advantages over other methods such as those depending on the eye, but faulty places in the photograph must be carefully avoided or eliminated by comparison with other photographs.

METHOD OF PLOTTING.

Curves were first made from the galvanometer deflections and the positions on the comparator. The intensities of the light transmitted by the negative were plotted as ordinates and the comparator readings as abscissæ, these plots being made while the measurements were being made, *i.e.*, plotting rather than recording the numbers. The intensities are merely relative, so that a convenient arbitrary scale was chosen to represent them. The positions of the mercury lines were located on the plot by observing the comparator reading for the smallest deflection of the galvanometer; thus the densest part of the line was taken as the proper position of the line. A setting could be made to the nearest tenth of a millimeter. Five to seven mercury lines were thus located on each plot. Knowing their wave-lengths to four significant figures their reciprocals were plotted (on another sheet) as ordinates against their recorded positions on the plot as abscissæ, and thus a calibration plot was obtained, giving the reciprocal wave-lengths for any comparator reading on the first plot. Using this calibration plot the final plot was obtained where the intensities of the light were plotted against the reciprocal wave-lengths. A new calibration plot was used whenever the mercury lines were found to be spaced differently due to different magnifications caused either by a change in the settings of the spectrograph or by a change in the camera adjustment. Final curves were made in this way for each of the twelve uranyl compounds.

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[1] The well-known, yellowish green fluorescence of these substances is of a color to which most photographic plates do not respond well. The most satisfactory of the numerous plates tested was found to be the polychrome plate made by the Eastman Kodak Company.

[2] J. O. Perrine; Thesis in M.S. in Cornell University Library.

[3] Kunz and Stebbins, PHYSICAL REVIEW, 7, p. 282.

In these plots a millimeter represents 2.5 frequency units,[1] and one tenth of a millimeter on the photographic plate. The accuracy of the data recorded in Tables I. to V. is such that the results are probably correct to within three frequency units. An estimated "probable error" is near one frequency unit. Typical curves are presented, greatly reduced, in Figs. 3, 4, 5 and 6.

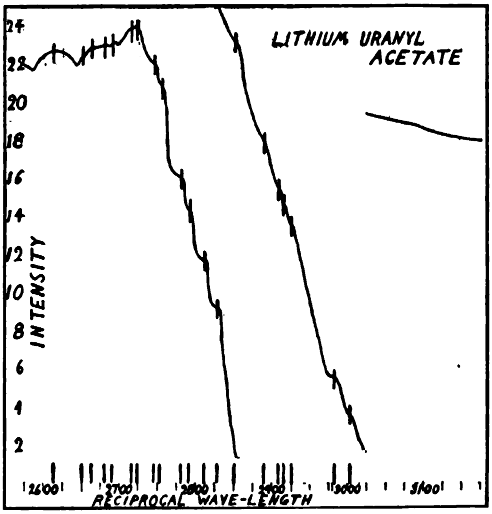

Fig. 3.

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[1] A frequency unit is such that 500 mμ corresponds to 2000 frequency units, *i.e.*,

$$\frac{1}{.000000500 \text{ in meters}} = 2000 \times 10^3.$$

Peaks in the curves represent regions of greater fluorescence. They are undoubtedly regions of greater absorption, and many of them coincide with absorption bands of these substances that have been located by

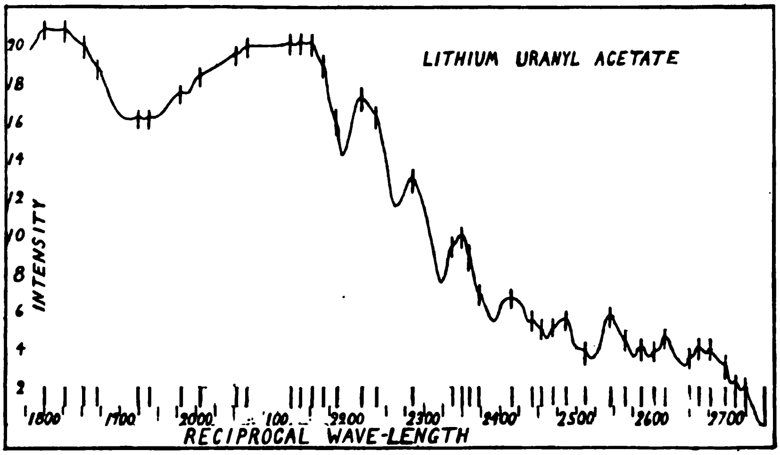

Fig. 4.

other methods. The data in the tables are arranged in two columns so as to show the agreement of the results obtained by this method and measurements made by other methods. The first column shows the

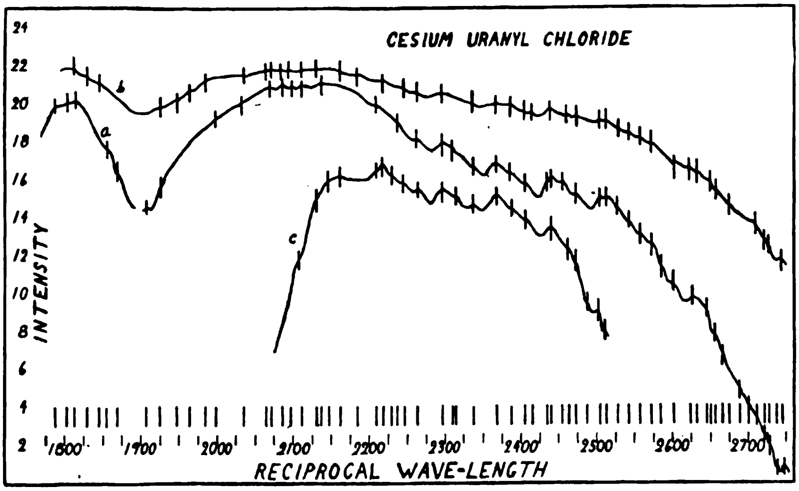

Fig. 5.

former, the second column the latter as published by Nichols and Howes. The photo-electric cell is so sensitive as to detect bands that are not apparent to the unaided eye. Data for these fainter bands seem to check equally well, therefore credence is given to these also. Wherever there is a marked difference in the direction of the curve such as to indicate a partially resolved band and wherever the main part of an unresolved band appears there is a short vertical line drawn through the curve, and these lines appear again at the bottom of the plot. The bands have been designated by the same symbols used by Nichols and Howes. In cases where bands could not be identified, symbols were assigned so as to agree as nearly as possible with those of the same class, *e.g.*, the acetates, nitrates, etc., as determined by Nichols and Howes.

Extension of the Absorption Region.

Some of the photographs show very distinctly that the absorption bands extend further into the ultraviolet region than it has been possible

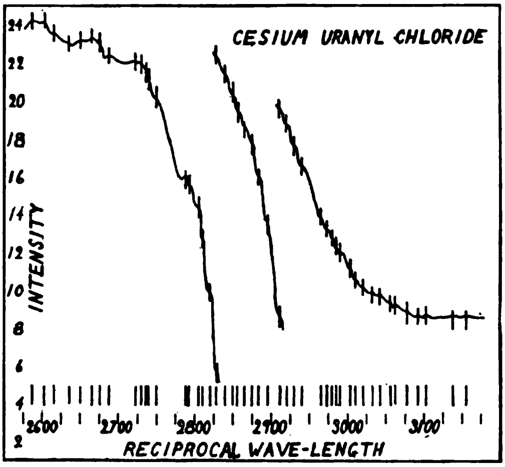

Fig. 6.

to go by the other methods. Cesium uranyl chloride is particularly rich in bands throughout the region covered by the photograph. It has been known that this substance is more fully resolved at ordinary temperatures than most of the other uranyl compounds. In order to see if the bands really extend as far as there is any fluorescence excited, a few long-time exposures were made, the range being 390 mμ to 310 mμ. A quartz-bulb nitrogen-filled tungsten lamp was used. An exposure of two hours was found to be sufficient to register all of the bands that could be recorded by the photographic plate. Further exposure only made the black part of the plate darker and made the detection of the bands by the photo-electric cell more difficult. In fact it was necessary to have regard to the time of exposure in all cases in order to obtain proper

Table I.

Bands Appearing in Two or More Curves for Cesium Uranyl Chloride.

Range 550 mμ to 370 mμ, approximately. See Fig. 5.

	Curve *a*, 1/λ.	Curve *b*, 1/λ.	Curve *c*, 1/λ.	Curve on Fig. 6.
B_1	1812	1810	....	
D	1925	1925	....	
E_2'	2032	2035	....	
d	2070	2072	....	
d'	2086	2085	....	
e_2'	2098	2095	....	
b	2113	2113	....	
b_2	....	2131	2130	
d	....	2148	2145	
d_2''	....	2162	2162	
d'	2210	....	2210	
d	....	2218	2218	
e_2''	....	2245	2245	
b_2'	2263	2263	2265	
d_2'	2298	2296	2297	
b_2	2337	2336	2337	
d_2	2367	2365	2368	
e_2''	2385	2388	2388	
b_2'	2405	2405	2405	
d_2	2440	2438	2440	
a_1'	....	2462	2464	
b_2'	2473	2475	2473	
d_2'	2505	2505	2503	
d_2	2512	2512	2510	
e_2''	2528	2530	....	
b_2'	2543	2543	....	
b_2	2557	2557	....	
d_1''	2572	2572	....	
d_2	2586	....	....	2586
e_2''	2600	2602	....	2602
c	....	2632	....	2633
d	....	2650	....	2650
e	2657	2657	....	....
a	....	2675	....	2675
b_2'	2687	....	....	2686
d_1''	2712	2710	....	....
d	2722	2722	....	2722
e	2730	2728	....	....

sensitiveness in measuring the plates. Too long exposures tend to fill up the places between the bands and destroy the contrast.

All of the twelve compounds were photographed for the range 390 mμ to 310 mμ, measurements were made, and the data plotted in the same manner as in the case of the first range. Since the first range extended from about 550 mμ to 370 mμ, there was an overlapping of about 20 mμ. This repetition aided in establishing the reality of the bands. Only for cesium uranyl chloride were there independent measurements made with the photo-electric cell from different photographs over the first range. These are plotted on the same sheet (Fig. 5). There is also a curve to show the effect of placing a screen between the substance and the plate

Table II.

Barium Uranyl Acetate.		Lithium Uranyl Acetate.		Uranyl Acetate.	
B. Values of 1/λ.	N. & H. Values of 1/λ, p. 161, 167.	B. Values of 1/λ.	N. & H. Values of 1/λ, p. 158, 164.	B. Values of 1/λ.	N. & H. Values of 1/λ, p. 149.
1805 I		1800 A		1788 E_1	1791 E_1
1830 D	1828 D	1827 C	1825 C	1803 F	1802 F
1862 H		1852 F	1852 F	1820 G	1817 G
1888 I		1870		1860 B	1857 B
1925 E	1923 E	1924 D		1913 H	1912 H
1943 G	1942 G	1938 F	1936 F	1965 E	1965 E
1975 I		1980 I		1988 G	1989 G
2018 F	2017 F	2005 D	2005 D	2028 B	2029 B
2032 H		2052 h		2039 C′	2039 C′
2070 C		2068 h′		2053 F_1	2056 F_1
2085 D	2086 D	2125 h	2124 h	2075 G	2073 G
2100 F	2101 F	2138 h′		2088 H	
2125 G′		2152 c′		2100 e′	
2155 c		2168 c		2120 f′	
2210 g′		2185 e	2185 e	2150 d	
2245 e′		2219 c′		2173 e′	
2275 gh	2276 gh	2238 c	2235 c	2210 i	
2305 c″		2285 c		2215 g	
2345 gh		2338 h		2223 d	
2365		2350 h′		2260 f′	
2395 e	2394 e	2360 c′		2270 k	
2420 gh	2419 gh	2373 c	2373 c	2281 i	
2450 f′		2415 h′		2303 c	
2475 g		2443 c	2446 c	2315 e′	
2488 gh	2487 gh	2455 f		2323 e	
2502 c		2470 e		2340 k	
2520 f′		2488 h′		2353 d	
2530 e″		2513 c	2515 c	2388 f	
2548 g		2545 h		2412 k	
2560 gh		2565 c		2445 c	
2568 c′		2586 c	2585 c	2465 e	
2578 c		2603 g		2490 i	
2600 e″		2610 e		2503 d	
2615 g		2618 h		2518 c	
2626 h′		2635 c		2538 e	
2632 gh		2650 c		2547 f′	

TABLE II.—*continued.*

Barium Uranyl Acetate.		Lithium Uranyl Acetate.		Uranyl Acetate.	
B. Values of 1/λ.	N. & H. Values of 1/λ, p. 161, 167.	B. Values of 1/λ.	N. & H. Values of 1/λ, p. 158, 164.	B. Values of 1/λ.	N. & H. Values of 1/λ, p. 149.
2665 e′		2663 c		2557	
2688 g		2678 e		2563 i	
2707 c′		2688 h		2576 d	
2728 f′		2698 h′		2585 c	
2738 e′		2711 c′		2593 e′	
2748 e		2724 c		2602 f	
2757 g		2743 g		2607 e′	
2770 gh		2750 e		2618 f′	
2790 c″		2778 c		2633 i	
2805 e′		2790 c		2638 g	
2815 e		2810 g		2653 c	
2843 gh		2828 h		2675 e	
2855 c		2850 c′		2680 x	
2867 f′		2889 e		2690 f′	
2877 e′		2907 h′		2697 k	
2888 e		2915 c		2708 g	
2905 h′		2925 c		2718 d	
2922 c′		2982 c		2740 f	
2930 c″		3003		2748 x	
2943 e′				2763 k	
2978 gh				2777 g	
2995 c				2789 d	
3030 e				2813 e	
3085 e′				2825 f′	
3122 c′				2838 k	
3148 f′				2848 g	
				2880 e	
				2923 d	
				2948 e	
				2973 k	
				3028 x	
				3057 g	
				3075 d	
				3118 k	
				3128 g	
				3143 d	
				3165 x	

with the hope of screening off some of the visible light diffusely reflected from the substance. This procedure was however not satisfactory. One purpose of the three plots (or curves) for cesium uranyl chloride is to show how well the bands check. The data are given in Table I. Bands that appear in two or more curves are given in parallel columns. It can be seen that the differences are few in number and are well within the experimental error.

Discussion of Results.

In Tables II. to V. comparison is made with former data obtained when the substance was at the temperature of liquid air, – 185° C. This seems justifiable because of the fact that some of the compounds are partially resolved at room temperature, so that the components, which are separated quite well by the relatively large dispersion of the spectrograph, show up well when measured by the photo-electric cell.

A comparison of the results obtained by the present method with those of other methods seems to establish the fact that *the position of the absorption bands can be determined by the fluorescence that the absorption gives rise to,* a fact already established by Howe[1] in the case of certain phosphorescent sulphides. Not all absorption bands may have the

Table III.

Potassium Uranyl Nitrate.		**Potassium Uranyl Chloride.**		**Rubidium Uranyl Sulphate.**	
B. Values of 1/λ.	**N. & H. Values of 1/λ, p. 139.**	**B. Values of 1/λ.**	**N. & H. Values of 1/λ, p. 90–93.**	**B. Values of 1/λ.**	**N. & H. Values of 1/λ, p. 174, 178.**
1795 D	1794 D	1761		1810 I	1812 I
1823 I	1824 I	1787 A_1	1785 A_1	1822 A′	
1860 B	1862 B	1815 C_1	1816 C_1	1842 C	1844 C
1978 E	1976 E	1945 E_2'	1940 E_2'	1872 F	1872 F
2005 J	2007 J	1987 C_2	1988 C_2	1907 A′	1908 A′
2070 F	2069 F	2012 d_3	2014 d_3	1948 E	1947 E
2093		2085 d_3		1957 F	1955 F
2127 d		2155 d_3	2155 d_3	1990 A′	1992 A′
2162 f		2237 e_2'		2012 C	2011 C
2188 l′		2268 c_2'	2264 c_2'	2063 b_1	2066 b_1
2268 d	2269 d	2335 c_2'	2333 c_2'	2078	
2337 d		2375 e_2'	2375 e_2'	2093 e_1	2096 e_1
2372 f	2369 f	2390 a	2392 a	2133 b_1	2137 b_1
2394 l′	2397 l′	2456 a_1	2456 a_1	2165 e_1	
2425 j		2468 c_2		2190 g	2188 g
2450 k		2477 c_2'		2205 b_1	2206 b_1
2492 j		2530 a_2''	2533 a_2''	2238 e_1	
2522 k		2548 c_2'		2268 h	2267 h
2535 l′		2595 a_1	2595 a_1	2282 c_1	
2563 j		2613 c_2'		2300 d	2301 d
2580 f		2626 d_1		2322 g_1	2322 g_1
2605 l′		2655 e_2'		2340 h	2341 h
2618 d		2665 a_1		2375 e_1	2375 e_1
2637 j		2675 c_2		2410 h	2409 h
2655 f		2698 d_1		2420 b_1	
2675 l′		2726 e_2'		2430 c	
2703 j		2737 a_1		2450 e_1	2450 e_1
2722 f		2755 c_2'		2482 h	
2745 l′		2782 d_3		2498 c_1	

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[1] Trans. Am. Philos. Soc., LVI., p. 259 (1917).

TABLE III.—*continued.*

Potassium Uranyl Nitrate.		**Potassium Uranyl Chloride.**		**Rubidium Uranyl Sulphate.**	
B. Values of 1/λ.	**N. & H. Values of 1/λ, p. 139.**	**B. Values of 1/λ.**	**N. & H. Values of 1/λ, p. 90–93.**	**B. Values of 1/λ.**	**N. & H. Values of 1/λ, p. 174, 178.**
2757 d		2800 b_1'		2522 e_1	
2798 k		2807 a_1		2550 h	
2813 l′		2818 c_2		2572 c	
2853 f		2835 d_1		2585 d	
2883 l′		2850 d_2		2606 g_1	
2898 d		2876 a_1		2622 h	
2915 j		2887 c_2		2637 c_1	
2928 f		2898 c_2''		2653 d′	
2953 l′		2918 d_2		2667 e_1	
2983 j		2939 b_1'		2680 g	
3032 d		2950 c_2		2705 c_1	
3050 j		2968 c_2''		2715 c	
3075 k		2998 e_2'		2724 d	
3100 d		3018 a_1		2738 e_1	
		3042 d_1		2745 g_1	
		3080 b_1'		2757 h_1	
		3100 c_2'		2782 c_1	
		3128 d_2		2803	
		3151 a		2820 g	
				2838 b_1	
				2855 c	
				2898 h_1	
				2915 c_1	
				2930 c	
				2949	
				2978 b_1	
				3000 c	
				3040 h_1	

power of exciting fluorescence, and, if so, such bands would not appear on the plate. This may explain why some bands are missing by this method. Most of the known bands do appear however and many more besides. Where formerly the absorption spectrum was observed only between 490 mμ and 380 mμ, approximately, *the range is extended by this method in both directions*, *i.e.*, 550 mμ to 322 mμ, or through a frequency range of 1800 to 3100. In the extension toward the shorter wave-lengths the bands readily fall into the series already determined, a fact which strengthens the belief that all regions showing fluorescence really serve to locate absorption bands.

In a few instances there seemed to be a new series starting somewhere near the middle of the complete absorption region, but more observations are needed to establish this if such is the case. Series of this sort are indicated by letters in the latter part of the alphabet. Again, there is some indication that the intensity of the members of the series varies as we go through the spectrum, resulting in more than one maximum. If this is true it may explain the apparent omission of a part of the series due to the faintness of the bands, as can be noted in some cases.

Reversing Region.

The so-called reversing region lies within the seventh, eighth and ninth groups of the fluorescent spectra, *i.e.*, 2,000 to 2,200 frequency units

Table IV.

Cesium Uranyl Sulphate.		Strontium Uranyl Acetate.		Sodium Copper Uranyl Acetate.	Mercury Uranyl Acetate.	Rubidium Uranyl Nitrate.
B. Values of 1/λ.	N. & H. Values of 1/λ, p. 175, 178.	B. Values of 1/λ.	N. & H. Values, p. 160, 166.			
1795 E	1794 E	1810		1820 C	1798 A	1788 D
1815 G	1813 G	2000 D	2004 D	1873 B	1812 B	1807 F
1845 B	1848 B	2050 H	2046 H	1975 A	1885 B	1840 K
1864 C	1861 C	2128 h′		2000 D	1980 C	1852 L
1903 G		2200 h′	2206 h′	2040 B	2015 c′	1910 I
1915 I	1913 I	2270 h	2274 h	2080 C	2030 c	1923 K
1952 D	1954 D	2287		2100 f	2085 c′	1960 D
1990 H	1993 H	2302 j		2128 b	2150 h	2045 D
2018 i		2337 h′		2152 h	2200 g	2095 K
2035 c′	2036 c′	2350 i	2350 i	2205 g	2218 h	2120 l′
2050 E	2052 E	2400 e″	2400 e″	2263 f_1	2252 e	2193 l′
2063 f	2061 f	2437 a		2275 g	2320 e	2218 δ
2080 h	2077 h	2516 j		2300 h	2365 c′	2270 d
2087 i	2085 i	2544 h′		2340 g	2405 h′	2295 h
2102 c	2104 c	2578 a		2365 h	2427 h	2338 d
2138 g		2613 h′		2410 g	2455 d	2360 δ
2147 g′	2144 g′	2655 j		2420 i	2493 i	2375 f
2165 a	2165 a	2680 e″		2473 f_1	2514 c	2390 l
2192 e		2695 h		2538 f_1'	2532 e	2402 l′
2222 g′		2718 a		2564 i	2563 i	2432 h
2232 a		2732 b		2573 h	2590 f	2473 l′
2280 g	2280 g	2770 i		2590 f	2602 e	2505 h
2290 g′		2799 b′		2605 f_1'	2622 g	2527 l
2307 a		2811 c		2620 g	2633 i	2550 d
2320 c′		2820 e″		2627 g′	2660 f	2570 δ
2352 g		2835 h		2632 i	2677 f_1	2585 f
2372 a		2875 b		2655 c′	2703 i	2595 l
2405 e		2903 h		2660 f	2707 h	2618 d
2428 g′	2427 g′	2928 a		2675 f_1'	2722 c	2626 e
2460 c′		2945 b		2680 f_1	2732 f	2635
2480 e′		2965 h′		2688 g	2738 d	2649 x
2500 g′	2498[1]	2975 h		2703 i	2755 h′	2655 f
2530 c′		3010 b′		2713 h	2770 c_1	2660 k

[1] No letters assigned.

TABLE IV.—*continued.*

Cesium Uranyl Sulphate.		Strontium Uranyl Acetate.		Sodium Copper Uranyl Acetate.	Mercury Uranyl Acetate.	Rubidium Uranyl Nitrate.
B. Values of $1/\lambda$.	N. & H. Values of $1/\lambda$, p. 175, 178.	B. Values of $1/\lambda$.	N. & H. Values, p. 160, 166.			
2543 e	2543[1]	3020 c		2728 f	2780 h	2670 l
2550 e'		3093 c		2753 f_1	2799 f	2680 l'
2568 g'	2567[1]			2770 i	2823 f_1	2698 e
2578 i				2780 h	2835 g	2712 h
2595 c				2793 c'	2850 h	2730 k
2605 d_1				2813 f_1'	2898 h'	2743
2615 e	2613[1]			2835 g'	2910 c_1	2750 l'
2626 f'				2850 h	2921 h	2755 d
2643 g'				2863 c'	2960 f_1	2770 e
2675 d_1				2876	2978 c_1	2780 S
2692 e'				2903 g'	3015 f	2802 k
2703 g				2922 h	3050 c_1	2822 l'
2726 a				2934 f	3170 f_1	2827 d
2756 e				2968 g		2835 e
2770 g				3005 f		2859 x
2789 i				3040 g'		2865 f
2820				3068 c'		2870 k
2850 g'				3097 f_1		2898 d
2874 c				3168 f_1		2925 h
2885 d_1						2939 k
2906 e'						2953
2920 g'						2965 d
2928 i						2988 S
2947 c						3002 x
2975 e'						3010 k
2993 g'						3028 l'
3001 i						3045 e
3026 d_1						3075 f
3052 g						3089 l
3068 i						3118 e
3133 g'						3139 x
3168 d_1						3150 k
						3173 l'

approximately. This region is extended further toward the long wave lengths if credence is given to the bands herein contained and if these bands are due to absorption, for, if any point on the plate containing the fluorescent material is being excited to fluorescence by the absorption of light of a particular wave-length, this absorption being due to the fluorescent material itself, there is evidently a reversal wherever the wave-length of the exciting light is equal to the wave-length of a band of the fluorescence spectrum. In the tables there are shown several bands agreeing well with the bands of the fluorescence spectra, *i.e.*, as well as

Table V.

Cesium Uranyl Chloride.

B. Values of 1/λ.	N. & H. Values of 1/λ, p. 90–93.	B. Values of 1/λ con.	N. & H. Values of 1/λ.	B. Values of 1/λ con.
1785 E_2'		2405 b_2'	2405 b_2'	2788 d_2'
1812 B_1	1810 B_1	2409 b_2	2410 b_2	2793 d_2
1828 C	1828 C	2415 b_3	2416 b_3	2804 e_2'
1845 D_1	1843 D_1	2435 d_2'	2436 d_2'	2810 e_2''
1855 D_2'	1854 D_2'	2440 d_2	2441 d_2	2819 b
1868 E_2''	1866 E_2''	2455 e_2		2828 b_2'
1906 B_3		2462 a_1'		2839 b_3
1924 D	1924 D	2474 b_2'	2476 b_2'	2850 d
1950 E_2''	1950 E_2''	2489 c		2857 d_2'
1963 A_2	1964 A_2	2505 d_2'	2509 d_2'	2865 d_2
1985 B_2	1985 B_2	2512 d_2	2513 d_2	2874 e_2'
1998 C_1	1998 C_1	2528 e_2''	2530 e_2''	2884 e_2''
2032 E_2'	2030 E_2'	2543 b_2'		2895 b_2'
2065 c	2064 c	2557 b_3		2911 c
2070 d'	2071 d'	2572 d_1''		2920 d
2085 d_2'	2086 d_2'	2586 d_2	2585 d_2	2930 d_2'
2098 e_2'	2100 e_2'	2601 e_2''		2940 d_2''
2107 a		2615 b_2'		2966 b_2'
2113 b	2114 b	2625 b_3		2973 b_2
2131 b_3	2132 b_3	2632 c		2980 b_3
2137 c_1'	2135 c_1'	2645 d_2'		2984 c
2147 d	2146 d	2650 d_2		2990 d
2162 d_2''	2164 d_2''	2657 e		3003 d_2
2185 b	2184 b	2665 e_2''	2670 e_2''	3010 d_2''
2210 d'	2212 d'	2675 a	2674 a	3020 e_2''
2218 d		2680 b		3032 b
2230 d_2	2229 d_2	2687 b_2'		3043 b_2
2238 e_2'	2239 e_2'	2693 b_2		3055 c
2245 e_2''	2245 e_2''	2702 c		3062 d
2263 b_2'	2263 b_2'	2712 d		3077 d_2''
2297 d_2'	2296 d_2'	2722 d_2		3092 e_2''
2310 e	2310 e	2730 e		3102 b
2315 e_2	2314 e_2	2736 e_2'		3137 d_2'
2337 b_2		2740 e_2''		3155 e_2'
2368 d_2	2369 d_2	2748 a		
2388 e_2''	2389 e_2''	2750 b		

the precision of the work warrants. These therefore indicate more reversals than have been heretofore obtained, and that the number of reversals in any one series is not limited to one, but may be as great as two or three.

It is rather curious that most of the new reversals are on the long wave-length side of the "reversing region" as given by Nichols and

Howes. In the cases of potassium uranyl chloride and rubidium uranyl sulphate none of the reversals by this method has been observed by other methods. This is true with cesium uranyl chloride, excepting the series E_2''. The methods give results that agree in series F of cesium uranyl sulphate. It must be admitted however that more data are needed in order to confirm or disprove the existence of the new reverasls. In cases where several photographs were made for the same substance there is a close agreement between the independent measurements, so that one is convinced that the method is capable of giving results quite comparable with those obtained by other methods.

The following table (VI.) shows the reversals of the bands in the various substances studied. The wave numbers in the first column are from Tables II. to V., and those to the right are from the tables given by Nichols and Howes on the pages indicated. Values in parentheses indicate that the corresponding band of the fluorescence spectrum is missing, or that it is not recorded by them. References are also missing for mercury uranyl acetate, sodium copper uranyl acetate, and rubidium uranyl nitrate, and they are therefore not included in the table.

TABLE VI.

Reversals of the Uranyl Bands.

Reversals by Present Method.		**Reversals Observed by Nichols and Howes.**
	Barium uranyl acetate	(Pages 161, 167)
Series		
D	reverses at 1830 and 2085	E reverses at 2009
F	" " 2018 " 2100	
	Potassium uranyl chloride	(Pages 88–101)
Series		
E	" " 1925	
G	" " 1943	
(H)	" " (1862) " (2032)	
(I)	" " (1805) " (1888) and (1975).	
	Lithium uranyl acetate	(Pages 158, 164)
F	reverses at 1852 and 1938	F' at 2105 reverses approximately with f' at 2109.
C	" " 1827	
D	" " 2005 " (1924)	
	Strontium uranyl acetate	(Pages 160, 166)
D	reverses at 2000	
H	" " 2050	
	Uranyl acetate	(Page 149)
E	reverses at 1788	
F'	" " 1803	
G	" " 1820, 1988 and 2075	
H	" " 1913 (2088)	
B	" " 1860, 2028	
E	" " 1965	
C'	" " 2039	
F'	" " 2053	

TABLE VI.—*continued.*

	Cesium uranyl chloride		(Pages 88–101)
E_2''	reverses at (1785), 1868, 1950, 2032	B	reverses at 1974
B	" " 1812	C	" " 1993
C'	" " 1828	D	" " 2005
D'	" " 1845	E	" " 2026
D_2'	" " 1855	A	" " 2037
D	" " 1924	E_2'	" " 2030
A_2	" " 1963	E_2''	" " 2034
B_2	" " 1985		
C_1	" " 1998		
A_1	reverses at 1787	B	reverses at 1969
C_1	" " 1815	C	" " 1984
E_2'	" " 1943	D	" " 2004
C_2	" " 1987	E	" " 2022
		A_2	" " 2039
	Potassium uranyl nitrate		(Page 139)
D	reverses at 1794		
I	" " 1824		
B	" " 1862		
E	" " 1976		
J	" " 2007		
F	" " 2069		
	Cesium uranyl sulphate		(Pages 173, 178)
E	reverses at 1795	F	reverses at 2061
G	" " 1815, (1903)		
B	" " 1845		
C	" " 1864		
I	" " 1915		
D	" " 1952		
H	" " 1990		
F	" " 2063		
	Rubidium uranyl sulphate		(Pages 174, 178)
I	reverses at 1810	E_1	reverses at 2028
A'	" " (1822), 1907, 1990	F	" " 2038
C	" " 1842, 2012	G_1	" " 2045
F	" " 1872, 1957		
E	" " 1948	G	" " 2049

SUMMARY.

Fluorescence is excited by wave-lengths of light between 550 mμ and 200 mμ, approximately. The intensity and range of excitation depends upon the substance.

There are three types of excitation observed:

1. Continuous, but variable in intensity, between 550 and 200 mμ.
2. Continuous, but variable in intensity, between 550 and 350 mμ.
3. Discontinuous, exhibiting a gap between 350 and 325 mμ, otherwise like type 1.

The range of the absorption spectra of twelve uranyl salts is extended to 550 mμ and to 320 mμ by the method herein discussed, a method which makes use of the fluorescence excited by dispersed ultraviolet light, observing that wherever greater absorption takes place greater fluorescence results therefrom.

It is desirable to continue the work on the uranyl salts by this method, especially in the reversing region, because it is here that information can doubtless be obtained about the real mechanism of fluorescence.

The gap at 350 to 325 mμ in case of a few substances noted is rather curious. No explanation is given, but further study of this type of excitation is desirable. It was observed that one of the uranyl compounds, namely sodium uranyl cobalt acetate, appeared to the eye to give this type of excitation, but it was not studied photographically because of the relatively weak fluorescence produced.

The writer wishes to express his gratitude to Professor Ernest Merritt under whose guidance this work has been performed.

PHYSICAL LABORATORY,
CORNELL UNIVERSITY.

SPECTRA OF HYDROGEN, NITROGEN AND OXYGEN IN THE EXTREME ULTRAVIOLET.

By J. J. Hopfield.

Synopsis.

Spectroscopy of Extreme Ultraviolet.—A method which has been developed of coating *films* with an emulsion suitable for work in this region is described in detail, and also an *oil-cooled discharge tube* of the internal capillary type which will stand an input of 2.25 KW and thus reduce the time of exposure and consequent fogging of the films from 10 to 100 fold. *Transparency of oxygen, nitrogen and air between 500* and *1,800* Å. was investigated. In a vacuum spectrograph with a grating of 50 cm. radius these gases were found to transmit light of from 1100 to 1225 Å. even when at a pressure of 3 cm. At around 1 mm. spectrum lines were photographed from 800 to 1,800 Å. and with oxygen at 0.001 mm., the spectrum was photographed to 430 Å. These gases, then, are not as opaque to light in this region of the spectrum as has been generally supposed.

Spectrum of discharge through hydrogen, 1,220 to 885 Å. The ultraviolet limit is the same for both continuous and disruptive discharges. Four spectrograms are reproduced and the wave-lengths are given for 90 lines below 1,059 Å., presumably due to hydrogen, as a continuous stream of pure gas was supplied. The resonance line was found superimposed in the fourth order on the H_β line; hence its wave-length is 1,215.68 ± 0.03 Å. This coincidence confirms the Bohr formula for this line, which is the first of the Lyman series.

Spectrum of Discharge through Nitrogen, 1,750 to 835 Å.—The continuous discharge gives chiefly the band spectrum of nitrogen, which is extended to 1,026 Å., the wave-lengths of 19 bands below 1,385 Å. being given. The wave-lengths of 50 new lines obtained with the disruptive discharge are also given and four spectrograms are reproduced.

Spectrum of Discharge through Oxygen, 1,863 to 507 Å.—Wave-lengths of about 100 new lines obtained with a disruptive discharge are given and six spectrograms are reproduced. *When mercury vapor was present* about 15 additional lines extending to 433 Å. were obtained.

Explanation of fluorescence observed around aluminum spark in air by Lenard in 1910, to a distance of 4 cm., may depend on the transparency of air to light of wave-length 1,000 to 1,400 Å.

Introduction.

It has long been assumed by investigators in the extreme ultraviolet, that most gases, and especially oxygen are opaque in this region. As a consequence it was believed that it was practically impossible to study the ultraviolet spectrum of oxygen under the conditions which usually exist in a vacuum grating spectrograph. About a year ago, the author, supposing oxygen to be opaque, attempted to get its spectrum by using two gases, the one hydrogen and the other oxygen. These gases were kept localized, the opaque one filling only the discharge tube, and the transparent one, hydrogen, the receiver. This was accomplished by suitably directing the two currents of gas.[1] The method was successful and suggested that after all oxygen might be transparent in the extreme ultraviolet. Following up this experiment was another in which both receiver and discharge tube were filled with oxygen, and in this case an extensive spectrum was obtained.[2] The spectrum of air also was obtained. This of course was expected in view of the transparency of nitrogen to 975 as found by Lyman,[3] and the now-established fact of the transparency of oxygen in this region.

There seems to be no especial difficulty, once the ultraviolet technique is acquired, in getting the spectrum of oxygen, and thus showing its transparency by obtaining its spectrum in the ordinary manner. In the progress of this research equipment was developed which when applied to the spectra of hydrogen and nitrogen yielded results that extended the spectra of these two gases. Other points of significance regarding these spectra were also brought out, hence these spectra as well as those obtained with oxygen will be described in this paper.

APPARATUS.

Most of the apparatus used was that ordinarily employed by investigators in this region of short wave-lengths, that is: a vacuum grating spectrograph, the necessary vacuum pumps, mercury traps, pressure gauges, generators for the gases used, driers, etc. The spectrograph, designed by E. P. Lewis and built in the department shop, consists of a sector-shaped cast brass box and holds at the smaller end, a concave grating of 50 cm. radius of curvature. This grating is of exceptionally fine quality. Within the larger end is a film-holder carried on a movable stage. This stage may be raised or lowered by rotation of a screw through a ground-glass joint, so that several exposures may be taken on the same film. This large end is also fitted with a broad flange against which the heavy glass lid is pressed. The plates were examined and measured on a Gaertner 20 cm. comparator. This comparator is the property of the Rumford Committee of the American Academy of Sciences, and was kindly loaned to the author by R. T. Birge for whose use the instrument was built. Furthermore, in order to fulfill the particular requirements of the research it became necessary to develop a special film for obtaining the photographs, and also a special discharge tube as the source of light. Since these last-mentioned articles of equipment may be found useful to other investigators, they are fully described in the next few paragraphs.

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[1] PHYSICAL REVIEW, **18**, 327, 1921.

[2] SCIENCE, **54**, 553, 1921.

[3] Astrophysical Journal, 43, 89, 1916.

Films.—The plates developed by Schumann could not be used to the best advantage on account of the large curvature of the focal field employed. Hence to obtain the spectrum in many orders in sharp focus, films sensitive to the ultraviolet were made. The method of making them is as follows:

Unexposed commercial films of the desired width are soaked in a solution of sodium thiosulfate until the emulsion is just dissolved. These films are then washed for three or four hours in running tap water, rinsed in distilled water and then dried.

Individual trays for the films are prepared as follows: Pieces of thin glass are cut one centimeter narrower and one centimeter shorter than the films to be prepared. (Old photographic plates from which the gelatine had been removed were used.) These glass strips, when fitted with two glass cross-pieces each, constitute the trays. These cross-pieces or feet, in order to hold the trays level on a levelled surface, are most conveniently made by drawing off pieces of *round* glass tubing, and labelling each pair of adjacent pieces with the same number by means of a file. The glass plate is then slightly warmed and a pair of these feet is stuck to it with warm red wax, care being taken to press them in contact with the plates. The spacing of the feet may be such as to divide the glass plate into segments of about the following ratios, 1 : 2 : 1. The diameter of the tubing employed may be any convenient one; about 5 millimeter for a 4 × 15 cm. plate is found satisfactory. To avoid disturbances due to surface tension, the shoulders of these short rods should not extend as far out as the edge of the trays. Mats of filter paper are cut to the size of the trays.

The trays with their mats (as many trays as films) are then mounted on a levelled table of glass. A good piece of window glass serves very well for this purpose if the films are not too large, otherwise plate glass is recommended. The mats, now on the trays, are each wetted with distilled water, about 10 c.c. being used for each 4 x 15 cm. mat. The films of the desired size are wetted in distilled water and placed upon the mats with the former emulsion side downwards. The following operations must now be carried out in a photographic dark room in brown light. The emulsion (a note on its preparation is given in a succeeding paragraph) about 20 c.c. per 5 x 16 film, is poured from a pipette over the film. If the emulsion does not immediately cover the film, it may be spread evenly by means of the pipette stem, and a little more added to replace any emulsion lost in the operation. The emulsion is then allowed to settle for three or four hours after which time it is carefully drained off, the films stripped from the paper and hung up to dry.

For assistance in draining, a rail of small glass tubing is waxed to the left-hand edge of the glass table, and a small glass rod, "L"-shaped, is used to catch the feet of the trays in order to pull them around to this tripping rail. These feet also serve as handles while removing the films. To pin up the films for draining and drying, it is convenient to have a horn-tipped tweezers with a longitudinal groove cut on the outside of one of the tips and this channel to end in a transverse notch across both tips, so that the groove is towards the operator and the notch uppermost when the film is held by the tweezers in the right hand. Then pinning, even in the dark, is a simple matter, and there is little danger of either dropping or marring the film in the process. It is detrimental to the film to grasp it with the tweezers too soon after beginning to drain for the reason that the undrained liquid forms a surface skin over the emulsion; a slight contamination from the tweezers ruptures this skin and as a result a streak may extend the entire length of the film. To avoid this and at the same time save a minute in this preliminary draining, one may have three or four trays at the tripping rail inclined on corks, and they then will be well drained when needed. When the films are thoroughly dried, they are warped with emulsion side inward and then placed on edge in boxes for storage. The sides of these boxes should have been fitted with corrugated filter paper so as to hold the films separated and in place. In this manner a number of films may be packed into each box. These smaller boxes may be put into a larger one and thus the films, now provided with twofold cover, are well shielded from light.

The advantage of having warped films is evident when one is using them, for if by accident one is dropped onto the floor it always alights on its back; other advantages are easy storage, ready adaptability for mounting, for measurement, or for reproduction.

The method described above is readily adaptable, with only slight modification, to making plates. Evidently the process is not one of delicate technique, for if one plate or film is spilled the rest are unharmed, and even it is not spoiled for the wet mat keeps its bottom dry of emulsion.

One may use any ordinary commercial developer if diluted three- or fourfold with cold tap water. It may be used at room temperature. Fresh films are not sensitive; they become so in about a week, and then seem to increase in sensitiveness with age.

In the preparation of emulsion, the method devised by Schumann[1] was employed with a few modifications, namely; a good quality of French pastry gelatine was used instead of Nelson's number one as recommended by Schumann, and only 50 to 60 per cent. as much as used by him, and the sensitizing temperature was varied between 60 and 40° C.

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[1] Baly, "Spectroscopy," p. 375.

The films thus made proved very satisfactory in getting the spectrum of oxygen. They were less satisfactory for the spectrum of air, and failed almost completely on account of fogging when a long exposure was used in an attempt to extend the spectrum of nitrogen. It soon became evident that in order to get the spectrum of any gas that easily ionizes or forms corrosive compounds that attack the film, a short exposure, much less than an hour would be necessary. At a given pressure, the amount of fogging seems to increase rapidly with the time of exposure whatever the strength of the current might be. (It may be stated that my observations confirm those of Lyman, in that there seems to be for minimum fogging a certain nice balance between the current density, the capacity and induction in the circuit, and it may be added the heat produced in the discharge tube. With such adjustment an exposure of two hours in oxygen at 0.04 mm. pressure gave no appreciable fog on the film.) Hence a more intense source of light was needed, and a continuous input of more than 200 watts would soon destroy an ordinary tube of the internal capillary type. Thus to meet the need of this greater power capacity for producing a more intense light, an oil-cooled tube such as shown in the figure was designed and used.

Discharge Tube.—Description of the figure. *A* opens into the receiver of the vacuum grating spectrograph, *B* is an outlet to the pumps, the kerosene oil used for cooling is pumped in at *C* and leaves at *D*, *E* represents an inlet for gases if one wishes to use it. The capillary constriction is a safeguard against any of the drying chemicals being forced into the discharge tube by any sudden rush of gas. *F* is a cylindrical electrode in contact with the glass and is thus cooled by it. A quartz window is at *G*. This is used for getting the quartz-mercury-arc comparison spec trum. The tube is made of pyrex, has a total length of 23 centimeters,

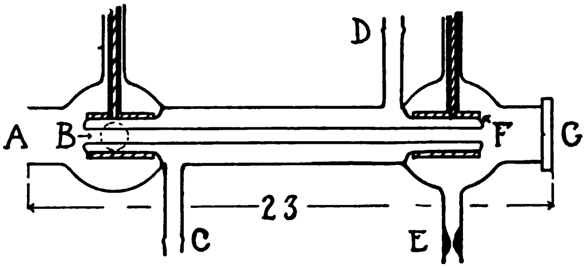

Fig. 1.

and is represented approximately to scale. This tube was found to have a power capacity of about 2.25 kw. It reduced the time of exposure from one or two hours to as many minutes and hence satisfactorily solved the problem of fogging.

METHOD.

The film is placed in the receiver. A piece of heavy plate glass with a border of especially prepared rubber grease is pressed over the opening and the oil pump started. After a half hour the pressure in the receiver is reduced to 0.04 or 0.05 mm. The receiver is then rinsed with a small quantity of the dried gas to be studied, and 4 or 5 cm. of the gas admitted and allowed to stand for an hour in order to "season" the film, for this shrinks somewhat on being exposed to the dry atmosphere of the receiver. The gas is then pumped out, and, while the spectrum is being photographed, a steady stream of gas is kept flowing through the receiver into the discharge tube, leaving via *B* to the pumps. Since the average exposure is but two or three minutes per spectrum, this may easily be done without using a prohibitive quantity of gas. By properly adjusting the intake and rate of pumping the pressure in the receiver may be kept at any desired steady value and at the same time a fast circulation maintained. When low working pressures are desired in the receiver, a mercury condensation pump is used, and a mercury trap cooled with liquid air keeps the mercury vapor out of the receiver. It is also necessary when working at low pressures to admit the gases through long capillary tubes.

DESCRIPTION OF PLATES.

All the photographs described below are reproduced in Plates I. and II., but necessarily many details are lost in the reproduction. It is hoped, however, that most of the essential features will be evident.

Plate I., Figures 1 and 2.—Hydrogen, direct current 320 milliamperes, 3 mm. pressure, circulation, 2 minutes' exposure. This film shows some of the series lines of hydrogen. The resonance line is shown in four orders. It is evident that a large current density brings out the series lines in the ultraviolet. This resonance line is shown self-reversed in the three higher orders, and in the fourth order the self-reversed portion coincides exactly with the sharp line H_β of the Balmer series. H_γ and H_δ also appear on the prints. This coincidence of the resonance line with H_β at once furnishes not only an accurate determination of the wavelength of the former, namely, one fourth of that of H_β, but also checks its value as derived on the Bohr theory. The first statement is strictly valid because the spectra are obtained under practically vacuum conditions, hence the wave-lengths as found by coincidence of orders need not

Physical Review, Second Series, Vol. XX.
December, 1922.

Plates I. and II.
To face page 578.

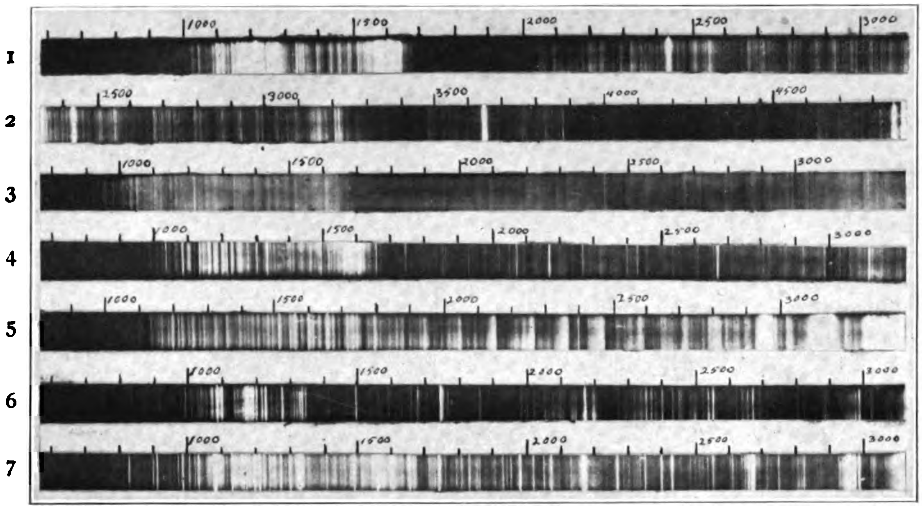

Plate I.

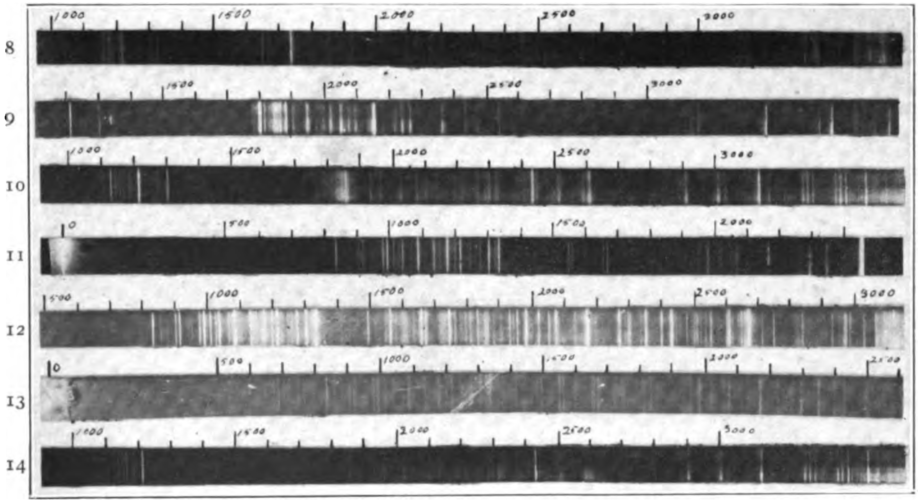

Plate II.

J. J. HOPFIELD.

be modified for the varying dispersion of the medium. The accuracy of the application of the Bohr theory to this resonance line may be seen by comparing the formula for its frequency with that giving the frequency number of H_β. The first is given by

$$\nu_1 = R\left(\frac{1}{1^2} - \frac{1}{2^2}\right)$$

and the last by

$$\nu_2 = R\left(\frac{1}{2^2} - \frac{1}{4^2}\right).$$

Hence one fourth the frequency number of the first is exactly the frequency number of the second. Thus the coincidence of the first order of the one line with the fourth order of the resonance line, as the theory would predict, has been found.

The wave-length of H_β as found by Curtis[1] and reduced to vacuum is 4862.677 Å. on the International System. Hence the wave-length of the resonance line is 1215.68Å. Owing to the unusually favorable conditions of observation, that is, a sharp line occurring in the middle of the reversed portion of a more diffuse line, it is thought that the probable error in this determination is about 0.02 or 0.03 Å. This indicates that the value attributed to this line by Lyman is too high by 0.3 Å., and that the value used by Millikan is more nearly correct. It is safe to assume, in the opinion of the author, that the best values of the other lines of the Lyman series are likewise the theoretical ones. Thus the first three that have been found by Lyman and which also occur on our plates (see Plate II., 12; Table VI.) have the following wave-lengths 1215.68, 1025.73, and 972.54 Å. These lines, which are readily obtained, may be used as standards in the ultraviolet where up to the present none have been established with an accuracy exceeding 0.1 Å.

Figure 3.—Hydrogen, direct current, 320 milliamperes, circulation, 8 minutes' exposure. This shows the extension of the secondary spectrum of hydrogen to 885.6 Å. The wave-lengths are recorded in Table I. Some of the lines recorded by Lyman[2] are also shown for the sake of comparison. (The wave-lengths in this table and subsequent ones were not measured in the expectation of great accuracy. It is hoped, however, that the individual values will be found accurate to at least 1 Å.) The continuous spectrum of hydrogen mentioned by Lewis[3] is shown on this plate in the region between 1680 and 1950 Å.

[1] Proceedings of the Royal Society of London, A 90, 605, 1914.

[2] "Spectroscopy of the Extreme Ultra-violet," p. 112.

[3] Science, 51, 947, 1915; Physical Review, 16, 376, 1920.

Table I.

Hydrogen.

λ.	I.	λ.	I.	λ.	I.
885.6	1	955.3	4	1006.1	3
889.2	1	956.1	1	1006.4	4
892.5	1	957.7	2	1007.9	4
895.3	1	959.4	1	1009.6	2
903.1	1	960.5	2	1011.0	3
905.3	1	962.5	1	1012.4	4
906.7	1	963.5	3	1013.4	1
908.9	1	964.8	1	1014.6	1
911.5	2	968.9	1	1016.2	5
912.7	1	969.8	2	1017.3	4
916.9	3	970.9	4	1018.6	4
917.8	2	971.8	1	1021.3	3
919.9	4	975.4	1	1023.9	4
921.1	1	977.2	8	1025.8	8
922.4	2	978.8	8	1027.3	3
924.3	3	981.9	5	1029.4	2
927.4	2	984.4	1	1031.0	7
928.8	2	985.2	2	1034.6	7
929.5	2	989.0	3	1035.5	1
932.0	2	989.9	2	1036.9	4
935.6	5	991.1	3	1040.4	7
941.9	1	992.0	3	1044.7	4
942.6	1	993.8	1	1045.5	5
944.3	1	995.9	2	1047.1	7
946.2	3	997.1	2	1048.0	7
949.8	2	998.4	1	1049.2	4
950.6	2	999.4	1	1051.2	5
951.9	4	1001.4	4	1053.1	6
952.9	2	1002.3	4	1056.1	6
954.4	4	1004.4	3	1059.2	4

Figure 4.—Hydrogen, disruptive discharge, 0.02 mm. pressure, circulation, 20 minutes' exposure, mercury arc spectrum superimposed. No extension of the ultraviolet spectrum is observed under these conditions. The lines at λ 835, and λ 900 and many of the strong lines that appear throughout the entire spectrum are due to air.

Figure 5.—Nitrogen, direct current 324 milliamperes, 3 mm. pressure, circulation, 2 minutes' exposure. Table II. This spectrum is found to be principally a band spectrum extending to λ 1025.8, but many

TABLE II.

Nitrogen, Direct Current.

Line Spectra with D.C.		Lyman, λ.	Bands Degrading towards Red, λ.	Bands Degrading towards the Violet, λ.
λ.	I.			
1329.5	3		1054.5	1025.8
1412.4	3		1164.3	1033.3
1493.2	6	1492.8	1183.6	1046.7
1494.7	5	1494.8	1194.3	1067.0
1561.1	6		1213.9	1072.7
1657.2	6		1244.2	1086.0
1742.9	6	1742.7	1256.0	1110.4
1745.3	5	1745.3	1288.7	1152.2
			1322.7	
			1353.7	
			1384.7	

lines also occur. Lyman had previously explored the band spectrum of this gas to 1385 Å. The following evidence is offered showing that this new spectrum is probably due to nitrogen: It does not occur in either hydrogen or oxygen under the same or under any other conditions, when presumably the same impurities are present in these gases as in nitrogen. Of the line spectrum, two pairs shown in this table were found by Lyman[1] and the pair at λ 1493 was attributed to nitrogen, while the second pair at λ 1743 he states with less assurance is probably due to the same gas. The reason for this lack of certainty on his part as to the source of the above pair seems to be the possible impurities that might have been torn from the tube by the disruptive discharge used by him. That this pair is of the same origin as the first pair is indicated in the present experiment by the fact that it is produced by direct current in nitrogen, whereas the metallic lines of the electrodes which always occur when a disruptive discharge is used, never occur in this milder form of excitation. The other lines shown in Table II. are also probably due to nitrogen.

That a high-current density, such as used here, brings out line spectra not shown when smaller currents are used, is evidently due not only to the greater degree of ionization which must necessarily exist in order to carry the greater current, but also to the greater degree of molecular dissociation present at the high temperature that exists in the tube.

The near ultraviolet and visible spectrum as far as the green shown on our plates has not yet been examined for new lines.

Figure 6.—Nitrogen disruptive discharge, 1.5 mm. pressure, circulation, 2 minutes' exposure. Table III. This spectrum is of interest in that

it shows that the transparency of the gas at this pressure exists to about λ 800. In parallel columns in the above table of wave-lengths are shown lines obtained by Lyman[1] in helium. In fact this table and subsequent ones contain all the lines, except two faint ones, obtained by him in helium. That his lines are due to air entering his spectrograph as an impurity, despite his great care in eliminating such impurities, rather than to helium, seems quite probable.

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[1] "Spectroscopy . . . ." p. 113.

Figure 7.—Nitrogen, disruptive discharge, 0.02 mm. pressure, circulation, 20 minutes' exposure. The lines found by Millikan[2] on the refrangible side of λ 700 and ascribed to this gas were not found, perhaps owing to the opacity of the gas, which seems even more opaque than oxygen in this region.

Plate II., Figure 8.—Nitrogen, disruptive discharge, 3.5 cm. pressure, no circulation, 2 minutes' exposure. This film was taken in order to test the transparency of nitrogen. It was fogged because of the active nitrogen formed in the discharge tube and which spread into the receiver.

Table III.

Nitrogen—Disruptive Discharge.

λ.	I.	Lyman, Helium, λ.	λ.	I.	Lyman, λ.
834.9	2	834.8	1328.0	1	
838.3	1		1329.7	1	
917.2	2	916.7	1331.0	2	
978.1	3	977.6	1335.3	15D	
990.8	2	990.2	1343.7	4	
992.3	4	992.0	1345.5	3	
1006.8	1		1346.6	3	
1011.0	2	1010.6	1361.0	1	
1026.4	2	1026.0	1378.1	1	
1037.7	4	1037.0	1379.3	1	1379.5 Al.
1085.5	40	1084.9 }	1412.3	4	
1093.8	1	1086.1 }	1463.6	1	
1097.9	3		1467.6	1	
1101.3	4		1493.1	8	
1135.3	4	1134.7	1494.9	7	
1144.1	2		1536.2	1	
1152.7	1		1548.2	1	
1164.8	3		1551.0	1	
1168.4	4 Doublet		1561.2	8	
			1573.3	1	

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[1] Astrophysical Journal, 43, 89, 1916.

[2] Proceedings of the National Academy of Sciences, 7, 289, 1921.

TABLE III.—*continued.*

λ.	I.	Lyman, Helium, λ.	λ.	I.	Lyman, λ.
1176.0	20 Complex	1175.5	1574.4	1	
1184.1	20 "	1176.3	1590.1	2	
1189.5	2		1593.2	2	
1191.3	1		1611.6	1	1611.8 Al.
1200.4	15	1199.8	1616.1	1	
1215.7	15	1216.0	1627.5	2	
1225.5	8		1629.1	2	
1229.0	6		1647.5	3	
1243.5	4		1650.0	4	
1247.8	3	1247.9	1657.2	8	
1258.9	1		1670.5	1	
1261.7	1		1675.8	6	
1270.3	2		1677.8	2	
1276.0	10				
1280.6	1		1703.5	1	
1300.6	1		1718.5	1	1718.3 Al.
1311.0	5		1740.2	5	
1319.6	5		1742.7	10	
1324.2	4		1744.9	8	
1326.9	1		1747.5	4	
			1751.3	6	

From considerations of the dimensions of the spectrograph used, and the pressure of the gas as stated above, it is evident that a layer of nitrogen 4.5 cm. thick and at atmospheric pressure is easily transparent down to 1070 Å. More will be said concerning this in a subsequent paragraph.

Figure 9.—Oxygen, direct current 320 milliamperes, circulation, 3 mm. pressure, 14 minutes' exposure. This plate shows clearly the absorption band of oxygen first observed by Schumann. In the neighborhood of λ 1300 is shown the transparent region whose less refrangible edge was located by Lyman[1] and whose more refrangible edge was found by the author at about λ 1000. The short wave-lengths shown in the plate are λ 1215.7, λ 1217.7, λ 1302.5, λ 1305.2, and λ 1306.4. The first is the resonance line of hydrogen and the others are probably oxygen lines. The last three lines might easily be mistaken for a triplet, except for the fact that their relative intensities vary with the nature of the discharge used. Thus with a disruptive discharge λ 1302.5 is strongest, while with direct current such as used here it is weakest. The last two probably

form a doublet. The bands near λ 1800 are presumably CO and O_2 bands.

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[1] "Spectroscopy of the Extreme Ultra-violet," p. 64.

Figure 10.—Oxygen, disruptive discharge, 1.5 mm. pressure, circulation, 2 minutes' exposure. Table IV. Besides the lines on the more refrangible side of the absorption band mentioned above, most of which are probably due to oxygen, this spectrum contains another item of interest, that is, a new absorption band for oxygen is shown beginning at λ 1000 and extending towards the shorter wave-lengths.

TABLE IV.

Oxygen Disruptive Discharge.

λ.	I.	λ.	I.
1036.8	5	1743.1	5
1083.7	4	1745.7	4
1109.7	4	1752.3	3
1128.4	8	1760.9	8
1129.4	5	1781.4	7
1130.3	4	1787.0	7
1132.3	10	1799.7	4
1142.1	5	1821.9	3
1143.8	7	1854.7	6 Al.
1147.5	7	1862.8	8 Al.
1149.2	3		
1158.7	5		
1167.7	7		
1168.5	5		
1189.7	5		
1215.7	15		
1217.8	10		
1277.7	8		
1302.5	10		
1305.2	8		
1306.4	7		

Figure 11.—Oxygen, disruptive discharge, 0.04 mm. pressure, circulation, 2 hours' exposure. Table V. Another type of discharge tube was used in obtaining this spectrum. This film is of especial interest because it extends the spectrum of oxygen to λ 507.2.[1] It also shows that the second absorption band of oxygen gradually fades away with reduced pressure. Even the first band, that is, that in the neighborhood of λ 1500 disappears rapidly as the pressure is reduced so that spectrum

lines begin to appear throughout its entire extent. It thus becomes evident that instead of oxygen being one of the most opaque gases in the Lyman region, it is perhaps one of the most transparent in the more

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[1] Some of these lines were found by Millikan and independently by the author by this distinctly different method.

Table V.

Oxygen, Disruptive Discharge.

λ.	I.	Millikan, λ.	Lyman (Helium), λ.	λ.	I.	Lyman, λ.
507.2	1	507.8		946.1	3	
538.1	1			954.4	1	
554.2	1	554.2		962.8	2	
580.5	1			972.3	1	972.7
599.6	1	599.5	599.0	977.6	10	977.6
				980.2	3	
608.4	1			989.9	10	
610.0	1	610.1		991.5	10	
616.5	1	616.7		1000.0	3	
625.0	1	625.2		1006.4	1	
644.5	1	644.0	643.7	1010.5	11	
673.3	1			1026.0	5	
685.7	2			1028.6	2	
703.0	2	703.1	702.4	1037.0	10	
704.1	1		703.5	1040.6	1	
718.9	3	718.5	718.2	1041.8	1	
763.5	1			1066.3	5	
764.5	1			1085.2	10	
765.4	1			1110.3	2	
776.2	1			1103.7	1	
787.9	2			1114.4	1	
790.4	2			1122.9	1	
796.9	3			1128.4	5	
833.7	8		796.8	1129.6	2	
834.5	4	834.0	833.4	1130.4	2	
835.1	10		834.8	1132.5	2	
859.0	5			1134.8	10	
879.9	2			1139.0	2	
883.3	1			1142.0	2	
884.3	1			1144.1	3	
889.7	5			1147.4	4	
904.7	10		904.6	1149.2	1	
916.4				1149.8	1	
917.8	15			1151.3	1	
928.8	1			1152.6	6	
923.9	3			1153.9	2	

Table V.—*continued.*

λ.	I.	λ.	I.
1164.7	1	1265.1	1
1167.	2	1267.7	1
1169.0	2	1269.8	1
1175.6	20	1272.6	1
1183.0	1	1275.6	2
1184.8	3	1277.5	4
1193.7	2	1280.7	1
1194.8	1	1286.6	1
1197.4	4	1288.7	1
1200.1	10	1290.3	1
1206.8	3	1295.1	1
1209.9	1	1296.9	1
1215.7	10	1299.2	1
1218.0	5		
1222.3	1		
1225.6	1		
12 0.6	2		
1239.1	4		
1243.0	3		
1247.7	10		

refrangible part of that region and in the beginning of the Millikan region. The table also gives, in parallel columns, the values of the wave-lengths found by the author in oxygen, those found by Millikan and attributed to oxygen, and those found by Lyman in helium. This experiment strengthens Millikan's assertion that the lines he observed are oxygen lines. Of course all the lines recorded in the table are not oxygen lines. Many are common to the spectrum of nitrogen, a few to the spectrum of hydrogen, and some arise from the impurities in the receiver. Still after the elimination of all of these, it is the opinion of the author, that there remain in the region between λ 800 and λ 1400 many strong oxygen lines.

Figure 12.—Oxygen, disruptive discharge, 0.02 mm. pressure, circulation, exposure 1 hour. It is hoped that this plate will show the short wave-lengths mentioned above better than Fig. 11. The spectrum is not as pure as the one described above.

Figure 13.—Oxygen, disruptive discharge, 0.001 mm. pressure, circulation, about 30 minutes' exposure. Table VI. In this experiment the mercury condensation pump was kept running and no attempt was made to keep the vapor out of the receiver and discharge tube. Since the pressure indicated above was read on a McLeod gauge, it represents the

TABLE VI.

Occurring in Oxygen with Mercury Vapor.

λ.	I.	Millikan, λ.
433.0	V.D.	
451.1	V.D.	
526.0	1	525.7
530.2	1	
533.5	1	
558.1	1	
574.5	1	
629.8	2	629.6
635.7	V.D.	
651.	1	
660.6		
671.8	3	
691.3	1	
747.5	2	
773.0	2	
788.1	1	

partial pressure of oxygen only. At this low pressure, many new lines were observed in the ultraviolet. These new lines are indicated in Table VI. Perhaps mercury and oxygen are the principal sources. Even a cursory examination of this plate shows that the lines near λ 600 are of intensity comparable with those of longer wave-length. This would indicate that in a strong discharge in oxygen these short waves are produced strongly with the rest, but of course are absorbed before they reach the plate.

Figure 14.—Oxygen, disruptive discharge, 1 cm. pressure, circulation, 15 minutes' exposure. This plate shows how transparent oxygen is in this region of transmission below its absorption band. Another plate was taken more recently at 2.5 cm. pressure, and 15 minutes' exposure. This latter shows practically the same lines as the above plate and with only slightly diminished intensity. Hence oxygen in layers of minimum thickness of 3.3 cm. has a narrow region of transmission, which includes the wave-lengths 1100 and 1217.7 Å. It has already been shown that nitrogen is equally transparent in this region in layers 4.5 cm. thick. Hence air has a remarkable transparency in this region of short wave-lengths, for if one uses as the basis of reckoning, the proportion of oxygen and nitrogen in the air, it is seen that the absorption equivalent of the above-mentioned thicknesses of oxygen and nitrogen when mixed in air is a layer 4.2 cm. thick. This fact recalls an observation of Lenard[1]

who detected a fluorescence about an aluminum spark in air that extended to a distance of 4 or 5 cm. from the source. The above-mentioned facts of the short waves of lengths 1100–1218 Å. being able to penetrate that thickness of air would explain the fluorescence. They probably are not the same rays that penetrated both quartz and fluorite as stated by him.

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[1] Sitz. Heidelberg Akad. d. Wiss. Abhand., p. 31, 1910.

It gives the author great pleasure to acknowledge his indebtedness to his teacher Professor E. P. Lewis, by whose suggestion this research originated, and to express his thanks to his friend Professor R. T. Birge, for his many kind suggestions.

DEPARTMENT OF PHYSICS,
UNIVERSITY OF CALIFORNIA.

THE VARIATION OF METALLIC CONDUCTIVITY WITH ELECTROSTATIC CHARGE.[1]

By F. Wenner, Nyna L. Forman, and A. R. Lindberg.

Synopsis.

Variation of Metallic Conductivity with Electrostatic Charge.—Last year Perkins reported a positive result. His experiment has been repeated, using a fine copper wire, 0.08 mm. in diameter, in series with a sensitive galvanometer, as the insulated secondary of a transformer. The galvanometer was found to read the same whether the potential of this wire was + 6,000 volts or − 6,000 volts with reference to the primary which was grounded. This *negative result* shows that the resistance of this wire is changed, if at all, by not more than one part in five million even when the potential gradient at the surface is raised to about 150,000 volts (root mean square value) per centimeter.

REFERRING to a paper by Professor H. A. Perkins, bearing the above title, we quote as follows from this journal, 18, p. 131, 1921.

"A simple conception of metallic conduction based upon moving electrons seems to justify the assumption that a negative charge should increase the conductivity of a circuit, and a positive charge should decrease it. This has been tested as follows: A primary coil of about 80 turns was wound upon a glass cylinder inside of which fitted a smaller cylinder similarly wound as a secondary. The primary was excited from a 60-cycle commercial circuit. The secondary circuit, carefully insulated throughout, included a moving coil galvanometer and was given an alternating charge from one terminal of a high tension transformer giving about 5,700 volts, the other terminal being grounded. The two coils wound upon glass acted as a condenser, so that a fairly large charge could be communicated to the insulated system.

"In operation the galvanometer was not affected by the charging potential, but the induced alternating current caused a slight vibration of the 'spot' on the scale, and if it reached too high a value (say 3 milliamperes) produced a small deflection always in the same direction, and due, probably to constriction of the helical portion of the suspension system. If, however, the induced current and the charging potential were both present, a deflection as high as 30 scale divisions was obtained, which indicated a direct current of about half a micro-ampere. This phenomenon behaved in a perfectly regular and definite manner, and reversed if the phase of the charging E.M.F. were reversed by interchanging the terminals of the transformer. A change of phase less than 180° produced proportional changes in the reading of the instrument."

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[1] Published by permission of the Director of the Bureau of Standards of the U. S. Department of Commerce.

An effect such as that just described would be of sufficient importance to require careful investigation and a modification of our notions of metallic conduction. However, before considering an investigation to establish quantitative relations justified, we thought it advisable to repeat the experiment to see whether or not we could observe an effect of the kind and order of magnitude claimed.

That our data might be comparable with that previously obtained, care was taken to use substantially the same test current and voltage. An exact duplication of conditions did not seem possible on account of the meagerness of the description, nor advisable on account of the possibility of introducing disturbing effects.

The test circuit was made up entirely of copper, and had a resistance of about 75 ohms. Of this about 60 ohms was of wire having a diameter of .08 mm. and so disposed as to receive very nearly the same surface charge as if straight and at a considerable distance from other conductors. This wire was silk-covered, but presumably this did not materially affect the results obtained. This circuit was electrically shielded at all points of mechanical support. The shield included the case of the galvanometer and the metal covering over the secondary winding of the transformer supplying the test current, both insulated from the circuit. The shield and the test circuit were electrically connected through two 20-watt, 125-volt carbon lamps symmetrically located with respect to the galvanometer so that the shield and the test circuit were always at substantially the same potential with respect to "ground." Only by this or a similar arrangement was it thought practicable to secure an effective insulation for the test circuit. The transformer supplying the test current had oil and glass insulation between the primary and secondary windings and a shield for the primary winding as well as for the secondary winding. The shield for the primary winding was connected to "ground." Inside the secondary winding and extending to a considerable distance beyond the ends was a laminated iron core, the outer laminations of which formed a part of the shield around the secondary winding. With this double shield, and glass and oil insulation, we have reason to think there was no appreciable change either in the conduction or the displacement current from one winding to the other, with changes in the phase between the current in and the voltage of the test circuit. The transformer supplying the voltage to the test circuit was a 5,500- to 110- volt, 40-to 80-cycle potential transformer. The 110-volt winding was connected to our 120-volt, 60-cycle power circuit, while one terminal of the 5,500-volt winding was connected to ground and the other to the shield of the test circuit.

Current for the test circuit was supplied from a small 60-cycle generator located in the laboratory and under the control of one of the observers. The test current was delivered from this generator to the test circuit by two transformers and regulated mainly by an inductance between the generator and the first transformer, which was of a commercial type. The second transformer was the one described above. The test current was approximately 2×10^{-3} ampere, and the sensitivity of the galvanometer was such that a change of 10^{-9} ampere gave a change in the deflection of 1.2 scale divisions. During the observations, conditions usually were sufficiently constant so that the deflection of the galvanometer could be read to about half a scale division.

As a result of the alternating current there was a broadening of the image amounting to 20 scale divisions and always a shift of the position of this band with respect to the position of the image when there was no alternating current in the circuit. This deflection was made small by making the "zero" correspond approximately with the position towards which the image moved as the result of the dynamometer action between the current in the coil and the current induced in the pole pieces and core. When 6,000 volts were applied to the test circuit there was regularly a quick motion of the coil amounting to about ten scale divisions, and then a return to zero in a time corresponding to the deflection period of the galvanometer. The reason for this was not obvious, but as it in no way interfered with the observations, we saw no reason for being especially concerned about it. A sectored disk on the fly wheel of the generator, illuminated by a metal filament lamp connected to the power system, furnished a stroboscopic means of showing relative changes in the phase of the current in and the voltage of the test circuit.

During the experiment the generator supplying the test current was run just slightly above or just slightly below synchronism with the power circuit so that there was a gradual shift in the phase between the voltage of and current in the test circuit. During the observations, usually the time required for a shift of one cycle was between 5 and 10 seconds or approximately the same as a free period of the galvanometer.

Observations consisted in noting changes in the phase and looking for corresponding changes in the deflection of the galvanometer. However, no changes in the deflection of the galvanometer, that is of the band image, corresponding with changes in the phase could be detected.

If, therefore, the observations are reliable, we may conclude that when the potential of a practically straight, .08 mm. diameter, copper wire, is changed from + 6,000 volts to − 6,000 volts, its resistance is changed, if at all, by not more than about one part in 5 million, or not more than two-tenths per cent. of that reported for the original experiment.

While the two experiments probably differ considerably in detail, they seem to be fundamentally the same. There should, however, have been a difference in the magnitude of the effect observed if the explanation given is correct, for the following reason. In the original experiment only that part of the test circuit having a small part of the resistance was so disposed that it could have had a high potential gradient at the surface, and that, for the most part, only on one side of the wire, which presumably was larger than .08 mm. in diameter. In our experiment the potential gradient at the surface of the .08 mm. diameter wire was about 150,000 volts (root mean square value) per centimeter. The surface charge was therefore about as large as could have been obtained in air without special precautions, with reasonable assurance that there was no corona, and this density was maintained over a part of the circuit having more than three-fourths of the total resistance. It seems therefore that we should have observed an effect larger possibly by a factor of the order of ten. Inasmuch as the effect if present at all in our experiment certainly was smaller by a factor of more than 500, we may conclude that quantitatively the results of the two experiments differ by a factor of more than 1,000. Since both experiments gave definite results, it seems that the cause or causes for this difference should have been evident. However, of the causes considered, none which seemed plausible should have escaped notice in either experiment. We therefore have no explanation to offer for the marked difference in the results obtained.

A limited experience with the apparatus used, some of which was not well suited to the purpose, and all of which was hastily assembled, leads us to think that by this method it should be possible to detect changes in the direct component of the current to better than one part in 5 million of the alternating current. Steadiness of conditions could be much improved by the use of more suitable sources of current and voltage, and by working at night or when heavy machinery is not in operation in the vicinity. The sensitivity might be increased or a larger test current used if a galvanometer better adapted to this purpose were employed. Further, by avoiding all points and sharp bends, the potential gradient over that part of the circuit having most of the resistance could be made somewhat larger without getting into serious difficulties on account of corona. Considering all factors which limit the accuracy of the observations it seems that an overall precision ten times that which we claim for our experiment might be realized. However, unless a plausible explanation is found for the negative results which we obtained, or the matter becomes of more importance than it seems to be at the present time, we do not think that we would be justified in attempting a greater refinement.

Department of Commerce,
Bureau of Standards,
Washington, D. C.,
June, 1922.

Note.—A copy of this paper was sent to Professor Perkins, who in reply states that he has found the cause for the large effect originally reported, and expects to publish soon a paper giving the results obtained in a more recent investigation.

RECIPROCAL DIFFRACTION RELATIONS BETWEEN CIRCULAR AND ELLIPTICAL PLATES.

BY JOHN COULSON AND G. G. BECKNELL.

SYNOPSIS.

Diffraction Patterns inside Elliptical Shadows Due to a Point Source of Light.—When a circular disc with its plane originally tangent to the light wave is rotated about an axis in its plane, the Arago spot changes to a figure with four cusps which move out along the axes of the elliptical shadow, two approaching the foci as limits and the other two going outside the shadow. These changes are shown by a set of photographs obtained with a disc 1.6 cm. diameter placed 2 meters from a pinhole 0.3 mm. in diameter and 5 meters from the photographic plate. The diffraction pattern was found to depend only on the ellipticity of the shadow whether produced by an ellipse or by an inclined disc. Each quadrant of the diffraction pattern was found to be associated with the quadrant of the shadow adjacent to it but on the opposite side of the major axis. Careful measurements of the photographs proves that in each case the diffraction pattern is the *evolute of the geometrical shadow*. The effect is as though each element of the edge of the shadow contributed a spot along its normal, the result being a *caustic curve of diffraction*.

INTRODUCTION.

EARLY in the nineteenth century Poisson[1] predicted that if the Huyghens-Fresnel theory was correct the light intensity behind the center of a small opaque disc illuminated by a point source should be about the same as though the disc were removed. Arago verified this experimentally using a disc about 2 mm. in diameter. In a later paper Arago states that the same phenomenon was discovered by Delisle in 1715.

Some of the more recent investigators, Croft, Arkadiew, and Hufford[2] have repeated and extended the work of Arago. However, none of the writers has drawn attention to the fact that a disc illuminated by a point source of light and placed perpendicular to the wave-normal, when gradually rotated about an axis in its own plane produces a succession of broadening diamond-like figures with concave sides; nor, have they drawn attention to the reciprocal figures produced by ellipses.

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[1] Poisson, Verdet, Leçons d'Opt. Phys., Vol. 1, Sect. 66.
Arago, Oeuvres Complètes, Vol. VII., p. 1.
Delisle, Mém. de l'anc. Acad. des Sciences, 1715, p. 166.

[2] Croft, W. B., Phil. Mag., Vol. 38, p. 70 (1894); Nature, Vol. 66, p. 354 (1902).
Arkadiew, W., Phys. Zeit., Vol. 14, p. 832 (1913).
Hufford, PHYS. REV., Vol. III., p. 241 (1914); Vol. VII., p. 545 (1916).

Apparatus and Method.

The discs were turned from brass, the edges beveled and then polished while on the lathe with a fine-grained oil-stone. The sizes ranged from .5 cm. in diameter to over 5 cm.

Very accurate ellipses were produced by a lathe method as follows: A circular cylinder of brass was sawed in two along a plane making the desired angle with its axis. A thin plate of hard-rolled copper was fastened between the sections of the cylinder by means of screws inserted from one end of the cylinder. The cylinder was then chucked in a lathe and turned down so that the minor axis of the elliptical section was equal to the diameter of the circle mentioned above. This elliptical section having been replaced by another sheet of the same material the cylinder was further turned down to such size that the major axis of the new ellipse was equal to the diameter of the disc.

Each of these plates was held at the center of a circular ring (about 20 cm. in diameter) by three No. 44 steel wires. This ring was fitted inside a second ring of slightly larger diameter, so as to slide into any position in its plane. The outer ring was mounted in such a manner as to permit of rotation about a horizontal axis as well as about a vertical axis. By means of clamping screws rotation about any one of the three axes could be made without disturbing the other two adjustments.

The mounted disc was placed in the path of a cone of light emanating from a pinhole source illuminated from behind by a self-regulating carbon arc and a system of condensing lenses. The shadow of the disc was received through a long tube, blackened inside, upon a photographic plate.

The distance between the photographic plate and pinhole was 7 meters, and that between pinhole and disc was 2 meters. The photographic reproductions shown here were produced by a pinhole about .3 mm. in diameter, and were made with a disc 1.6 cm. in diameter and with two ellipses, one having its major axis equal to the minor axis of the other and equal to the diameter of the disc.

Procedure.

The disc was adjusted until the Arago spot was sharply defined at the center of the circular shadow received at the position of the photographic plate. In this position the disc is perpendicular to the wave-normal. The sizes of the Arago spot and the circular shadow are indicated by No. 1, Plate I.

When the disc is rotated about an axis in its own plane, in this case a vertical axis, the Arago spot changes gradually into the series of expanding patterns mentioned before. These are illustrated by Plate I, Nos. 2 to 8, corresponding to angles of rotation of 10°, 15°, 22.5°, 30°, 37.5°, 45°, and 60° respectively. Any one of these figures may be duplicated by an ellipse, whose minor axis equals the diameter of the disc, cut from a circular cylinder at the corresponding angle and placed perpendicular to the wave-normal.

Plate I., No. 9 was produced by an elliptical plate cut at an angle of 37.5°, and placed in the normal position just described. It corresponds to No. 6 for the disc when turned through an angle of 37.5°. In this case the major axis of the ellipse is equal to the diameter of the disc. An ellipse similarly cut, but with its minor axis equal to the diameter of the disc, when placed perpendicular to the wave-normal produces Plate II., No. 10. It will be seen that this diffraction pattern corresponds in shape to that of Plate I., No. 9, and is proportional in size to the dimensions of the ellipse.

When this ellipse is rotated about an axis in its own plane until the shadow produced is a circle (in this case 37.5°) then the Arago spot appears at the center of the shadow, as shown in Plate II., No. 11.

Examination will show that in all cases where the four cusps of the diffraction figure appear within the shadow (Nos. 3, 4, 5, 6, and Nos. 9 and 10) the intensity of light is greatest at the cusps lying on the major axis of the elliptical shadow. This fact is important in the experimental analysis, an account of which is now to follow.

Plate II., No. 16, shows the diffraction pattern produced by an ellipse when a straight-edge in the same plane is made tangent to the ellipse at the end of the major axis, the plane of the ellipse being perpendicular to the wave-normal. The spear-like shadow cast from the point of tangency is directed to the *adjacent* cusp. But, if the straight-edge is made tangent at the end of the minor axis the pointed shadow is directed to the cusp lying on the *opposite* side of the major axis. This is shown by Plate II., No. 17.

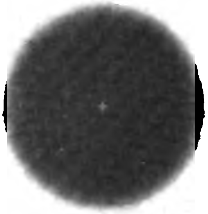
From the last two illustrations it is evident that each cusp lying on the major axis is produced by light emanating from the neighborhood of the *nearer* end of the same axis of the elliptical plate; while each of the cusps on the minor axis is due to light coming from the *farther* end of the latter axis. Furthermore, it has been observed that if the straight-edge is made tangent at successive points of the ellipse lying between the ends of the major and minor axes the extremity of the pointed shadow moves along the four-cusped diffraction figure. At any definite position of the straight-edge the bisector of the angle at the tip of the shadow is tangent to the diffraction figure and normal to the geometrical shadow.

If a circle replaces the ellipse the shadow from the point of tangency is directed toward the Arago spot at the center of the circular shadow.

PHYSICAL REVIEW, SECOND SERIES, VOL. XX.
December, 1922

PLATE I.
To face page 596.

1



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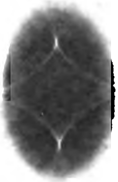

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9

JOHN COULSON AND G. G. BECKNELL.

(See No. 18.) If the disc and straight-edge be now rotated about an axis in their plane figures like Plate II., No. 16 and No. 17 are produced.

Attention may be drawn to the fact that the diffraction bands resulting from any combination of ellipse and tangent straight-edge differ in nature from the quadrantal diffraction figure produced by the ellipse alone. In the case of the former the bands are fringed with the prismatic colors, while in the latter case this color separation does not take place. It appears, also, upon photographing these figures with light of different colors that the dimensions of the main figures are independent of the wave-length.

Photographs 12, 13, 14, and 15 were taken while light was excluded from certain quadrants of an ellipse placed perpendicular to the wave-normal. In No. 13, an opaque screen shuts off all of the ellipse on one side of the major axis. Here the diffraction pattern lies *inside* the shadow of the screen. Hence, it is produced by the light coming from the *opposite* side of the major axis. If, now, the screen is so placed as to exclude light from all of the ellipse on one side of the minor axis the resulting pattern falls *outside* the shadow of the screen. Here, on the contrary, the light producing the diffraction comes from the *same* half of the ellipse into which the pattern falls. (See No. 14.)

Shutting off the illumination from two diagonally opposite quadrants of the ellipse produces the effect shown in No. 12. It will be observed that half of the complete diffraction figure is missing, and that the cusps do not appear. Furthermore, the portion of the figure lying in either quadrant is due to light from an adjacent quadrant, and not from the one diagonally opposite.

No. 15 completes the analysis concerning each quarter of the diffraction figure and the illuminated quadrant which produces it. Here the major axis of the ellipse stands lengthwise of the page, as it does in the other illustrations. In terms of the usual trigonometric convention light is excluded from all but the first quadrant of the elliptical plate, and the resulting diffraction is seen to lie only in the second quadrant of the geometrical shadow. This shows that each illuminated quadrant produces independently its own quarter of the diffraction figure and, therefore, that each of these quarters is due to light from its corresponding *adjacent* quadrant with respect to the major axis. Exactly similar properties are found in the case of the circle rotated through an angle.

The foregoing results may be summarized as follows:

1. The diffraction figures are quadrantal and symmetrical. As the eccentricity of the elliptical shadow gradually increases the cusps which lie upon the minor axis recede indefinitely, while those on the major axis

always lie within the shadow. As the eccentricity approaches zero the figure degenerates into a circular spot which becomes a geometrical point for a point source of light.

2. Each quarter of the diffraction figure is produced by light from the adjacent quadrant with respect to the *major* axis.

3. The intensity of illumination of the cusps lying on the major axis is always greater than that of those lying on the minor axis.

The facts here enumerated have suggested that the diffraction figures are the *evolutes* of an ellipse.

The evolute of a given curve is defined as the locus of its center of curvature. Every normal to the given curve is tangent to its evolute; hence, the evolute is the envelope of these normals.

In the case of an ellipse the cusps of the evolute which lie on the minor axis recede indefinitely with increasing eccentricity of the ellipse, while those on the major axis at the same time approach the foci. With decreasing eccentricity the evolute contracts and, in the limit, becomes a geometrical point. Furthermore, the envelope of the normals from any quadrant of the ellipse is the adjacent quarter of its evolute with respect to the *major* axis. Such an envelope corresponds to the curve formed by the rays as mentioned above.

The difference in the brightness of pairs of opposite cusps is accounted for if we consider the distance from the end of the major axis to the nearest cusp of the evolute, and the distance from the end of the minor axis to the further cusp on that axis. These distances are b^2/a and a^2/b respectively, where a and b are the major and minor semi-axes of the ellipse. Here b^2/a is always less than a^2/b. The distances just mentioned are, also, the radii of curvature of the ellipse at the ends of the major and minor axes.

The equation of the evolute corresponding to the ellipse

$$(x/a)^2 + (y/b)^2 = 1,$$

is

$$(ax)^{2/3} + (by)^{2/3} = (a^2 - b^2)^{2/3}.$$

The respective distances between the cusps lying on the major axis and those lying on the minor axis are:

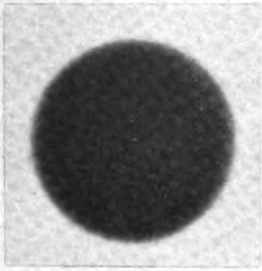
$$2x_0 = 2(a^2 - b^2)/a,$$

and

$$2y_0 = 2(a^2 - b^2)/b.$$

These distances when taken from the photographs permitted the calculation of a and b, which in every case were found to be the dimensions of the corresponding geometrical shadow.

PHYSICAL REVIEW, SECOND SERIES, VOL. XX.
December, 1922



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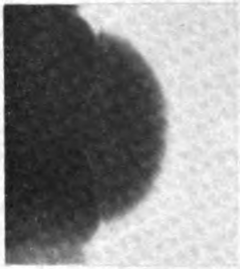

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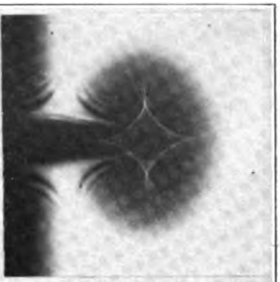

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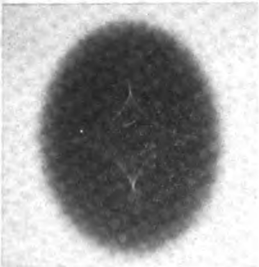

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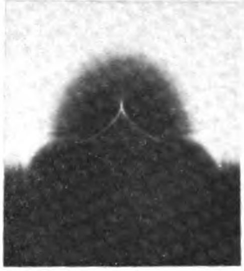

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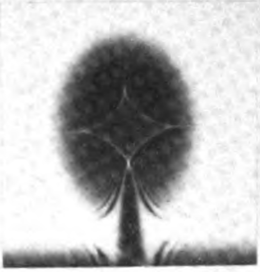

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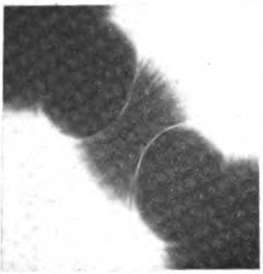

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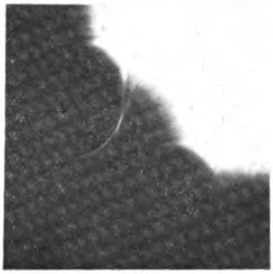

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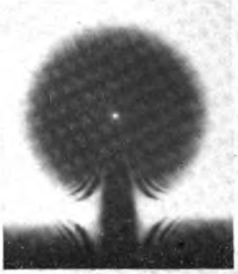

18

JOHN COULSON AND G. G. BECKNELL.

In order to show the complete coincidence between the diffraction figure and the evolute of the geometrical shadow it was necessary to produce photographically a large sharp-lined figure. This was done by using a disc of large diameter (5.11 cm.) and a very small pinhole source (.12 mm.). The disc was rotated 37.5° with respect to the wave-normal. The figure thus produced, which was about 7 by 8 cm., was projected optically, with a magnification of about 8 diameters, upon a sheet of coördinate paper. The values of x and y for one quadrant of this sharply outlined figure are the points represented by circles in Fig. 19.

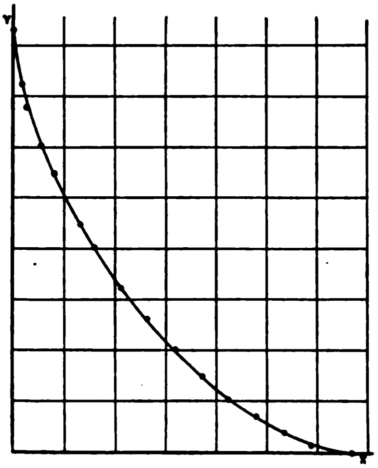

Fig. 19.

The curve itself is the computed evolute of the elliptical shadow. The agreement is well within the limits of observation.

The identity of the diffraction figure and the evolute of the geometrical shadow may be shown more readily from the following property of the evolute. The difference between the radii of curvature at any two points in the same quadrant of an ellipse is equal to the arc cut off of its evolute by the normals to the ellipse at the given points. Hence, it may be proved that the length of the quadrant of the evolute is equal to $(a^3 - b^3)/ab$.

The length of the quadrant of the evolute was measured for several figures (after enlargement) by rolling a self-recording wheel along the periphery of the curve. A planimeter-wheel was used for this purpose. The agreement between the length of the quadrant of the evolute thus measured and the quantity $(a^3 - b^3)/ab$ for the corresponding geometrical shadow was in each case less than one per cent.

The agreement between the diffraction figures produced by an ellipse and a rotated circle casting the same geometrical shadow is shown in the table. These data were taken from Plate II., No. 6, and No. 9, enlarged.

x.	y (Observed).	
	Rotated Circle.	**Ellipse.**
.000	1.330	1.340
.056	1.035	1.038
.127	.875	.851
.190	.720	.735
.253	.615	.631
.380	.445	.455
.507	.300	.314
.633	.197	.200
.760	.108	.108
.887	.044	.041
1.032	.006	.000
1.050	.000	

Attention may be called again to one of the important properties of the evolute. That is, the evolute is the *envelope of the normals* of the corresponding curve producing it. In the experiment with the straight-edge tangent to the elliptical plate it has been shown that for any given position of the straight-edge the median line of the corresponding pointed shadow is tangential to the diffraction figure and normal to the geometrical shadow of the plate. Hence, we may conclude that these diffraction figures constitute a family of envelopes, and corresponding to the caustics of reflection and refraction, that the figures here shown are the *caustics of diffraction.*

UNIVERSITY OF PITTSBURGH,
May, 1922.

HEAT FLOW IN A FINITE CYLINDER HAVING VARIABLE SURFACE TEMPERATURE.

By George E. Thompson.

Synopsis.

Equations of heat flow into finite circular cylinders when the surface temperature is changed either suddenly or at a uniform rate, are derived. In the first case the surface temperature of a cylinder whose temperature is initially uniform throughout is suddenly changed from 0 to V_0, kept there for a certain time and then suddenly changed to V_2 and kept there indefinitely. In the second case the surface temperature is changed to V_0, then is increased at a uniform rate from V_0 to V_2 and then is kept constant indefinitely. These two cases correspond roughly to the *changes occurring in two canning processes* and the theoretical curve for case two is found to agree roughly with an experimental curve obtained with a pint Mason jar filled with spinach by the "cold-pack" method.

SOME time ago the author of this paper[1] made a comparison of theoretical and experimental temperature-time curves for the flow of heat into finite circular cylinders—the cylinders under experimental test being cans of fruit or vegetables in the sterilizing process. The theoretical derivations of the formulæ for heat flow were not given in the published results at that time. Two formulæ not previously worked out were used. It is the purpose of this paper to present the derivation of these formulæ.

The two new cases worked out are as follows: In the first case the surface of the cylinder is maintained constant for a given length of time and then suddenly changed to a new value which is kept constant indefinitely. The initial temperature of the cylinder is considered uniform throughout. This corresponds to the conditions which are sometimes approximately maintained in a certain canning process—namely, where the can is heated in a bath of medium temperature for a limited time to expel the air and then, after sealing, is placed in a steam bath at sterilizing temperature. The second case considered corresponds closely to the conditions which apply to "cold-pack" canning methods. The surface temperature is assumed to increase linearly from a medium temperature to the sterilizing temperature and remain constant thereafter, the interior temperature being initially uniform throughout. We shall refer to these problems as Case I. and Case II.

Case I.—Let us use cylindrical coördinates, z representing the distance of any point from the center of the cylinder along the axis; r, the perpendicular distance of the point from the axis; l, the half length of the cylinder, and a, its radius. Only right circular cylinders will be considered.

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[1] Thompson, Journ. Ind. and Eng. Chem., July, 1919.

The problem, then, is to find a solution of the partial differential equation:

$$\frac{\partial v}{\partial t} = k\left(\frac{\partial^2 v}{\partial r^2} + \frac{1}{r}\frac{\partial v}{\partial r} + \frac{\partial^2 v}{\partial z^2}\right) \qquad (1)$$

subject to the conditions

(*a*) $v = v_0$ at $r = a$, $z = \pm l$ for $t < t_1$
(*b*) $v = 0$ at all points in the cylinder when $t = 0$
(*c*) $v = v_2$ at $r = a$, $z = \pm l$ or $t \geqq t_1$.

In the above expressions, v is the variable interior temperature; t, the time; and k, the diffusivity of the material constituting the cylinder.

We have to get the solution of the problem in two parts; first for $t < t_1$ and then for $t > t_1$. Carslaw has included the general solution for a steady surface temperature in his textbook, Fourier Series and Integrals, p. 324. This solution making $n = 0$ for symmetrical distribution is as given in Equation (3) where

$$A\mu,_{m.} = \frac{2\int_0^a J_0(\mu r)r\,dr \int_{-l}^{+l} \sin\frac{m\pi}{2l}(z+l)dz \int_{-\pi}^{+\pi} f(r,\theta,z)d\theta\,.}{\pi a^2 l J_1^2(\mu a)} \qquad (2)^1$$

By putting $n = 0$ since the distribution is symmetrical and $f(r, \theta, z) = 1$, this solution when modified to correspond to the conditions of our problem becomes for $t = t_1$,

$$v = -\sum_{\mu}\sum_{m=1}^{\infty} A_{\mu,\,m} v_0 e^{-Rt_1} J_0(\mu r)\,\sin\frac{m\pi}{2l}(z+l), \qquad (3)$$

where μ is a root of $J_0(\mu a) = 0$ and m is any integer,

$$R = k\left(\mu^2 + \frac{m^2\pi^2}{4l^2}\right),$$

and

$$A_{\mu,\,m} = \frac{1}{2}\cdot\frac{8(1 - \cos m\pi)l}{\pi a^2 m l J_1^2(\mu a)}\int_0^a J_0(\mu r)r\,dr, \qquad (4)$$

where $\int_0^a rJ_0(\mu r)dr$ may be replaced by its value $(a/\mu)J_1(\mu a)$.

In the second part of the problem where $t > t_1$ we have to solve the same differential equation subject to Condition (*c*) and that the interior temperature at $t = t_1$ is given by Equation (3). In order that the

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[1] Note that a factor, r, is omitted in the first integral of this expression in Carslaw's book; also b is a misprint for l in the denominator.

surface temperature may still be considered zero we shift the temperature scale by the amount $(v_2 - v_0)$ and get for the interior temperature distribution at $t = t_1$ the expression

$$f(r_1 z) = -(v_2 - v_0) - \sum_{\mu} \sum_{m=1}^{\infty} A_{\mu,\,m} v_0 e^{-Rt_1} J_0(\mu r) \sin \frac{m\pi}{2l}(z + l). \qquad (5)$$

By substituting this value of $f(r, z)$ in the expression at bottom of page 324 of Carslaw's textbook, we get, after simplifying,

$$A_{\mu,\,m}' = \frac{4(v_2 - v_0)(\cos m\pi - 1)}{m\pi(\mu a)J_1(\mu a)} - A_{\mu,\,m} v_0 e^{-Rt_1}, \qquad (6)$$

$$= -A_{\mu,\,m}(v_0 e^{-Rt_1} + v_2 - v_0). \qquad (7)$$

Hence we have

$$V' = \sum_{\mu} \sum_{m=1}^{\infty} A_{\mu,\,m}' e^{-R(t-t_1)} J_0(\mu r) \sin \frac{m\pi}{2l}(z + l). \qquad (8)$$

We should now increase all temperatures in (3) by v_0 and in (8) by v_2 in order to get the results into their final forms.

Case II.—As in Case I. we have to solve this problem in two parts; the first part to correspond to the condition that the surface temperature increases linearly with t until $t = t_1$. In the second part the surface temperature remains constant at a value v_2. Then

(*d*) $v = v_0 + Bt$ at $r = a$ and $z = \pm l$ when $t < t_1$,
(*e*) $v = v_2 = v_0 + Bt_1$ at $r = a$ and $z = \pm l$ when $t \gtreqless t_1$,
(*f*) and $v = 0$ for all points in the cylinder when $t = 0$.

Duhamel has given a theorem (Carslaw, loc. cit., p. 208) by means of which the solution for a variable surface temperature can be deduced from the solution for a steady surface temperature. According to this rule we are to use the solution which is given in equation (3) for a surface temperature maintained at zero. We are to replace the t in the surface-temperature function by λ and in the body temperature by $t - \lambda$. If the surface temperature be maintained at zero we have, after applying Duhamel's rule

$$V = (v_0 + B\lambda)[1 - v(t - \lambda, r, z)], \qquad (9)$$

where V is the function wihch is to be differentiated with respect to t and integrated with regard to λ between the limits 0 and t; and v is the function given in Equation (3) after $t - \lambda$ has been substituted for t.

The t-differentiation gives

$$\frac{\partial V}{\partial t} = (v_0 + B\lambda) \sum_{\mu} \sum_{m=1}^{\infty} RA_{\mu,\,m} e^{-R(t-\lambda)} J_0(\mu r) \sin \frac{m\pi}{2l}(z + l). \qquad (10)$$

After factoring (10) and integrating with regard to λ that part involving λ we have, after recombining,

$$\begin{aligned} V' &= \sum_{\mu}\sum_{m=1}^{\infty} A_{\mu,m}\left[v_0(1 - e^{-Rt}) \right. \\ &\qquad \left. + B\left(t - \frac{1 - e^{-Rt}}{R}\right)\right] J_0(\mu r)\sin\frac{m\pi}{2l}(z + l), \end{aligned} \tag{11}$$

$$\begin{aligned} &= v_0 + Bt \\ &\quad - \sum_{\mu}\sum_{m=1}^{\infty} A_{\mu\ m}\left[v_0 e^{-Rt} + \frac{B}{R}(1 - e^{Rt})\right] J_0(\mu r)\sin\frac{m\pi}{2l}(z + l). \end{aligned} \tag{12}$$

The coefficient of $v_0 + Bt$ is shown to be unity by placing $v = 1$ and $t = 0$ in equation (3). V' represents the interior temperature between $t = 0$ and $t = t_1$. After the surface temperature becomes constant at $t = t_1$ we have to solve another problem with V' as initial interior temperature and surface temperature $v_2 = v_0 + Bt_1$. In order to use the expression given by Carslaw (p. 324) we must reduce all temperatures by an amount $v_0 + Bt_1$ so as to make the surface temperature zero. The final result will then have to be increased by this amount. Substituting in Equation (2), $f(r, \theta, z) = V' - v_0 - Bt_1$ we get

$$2\pi C_m \int_{-l}^{+l} \sin^2\frac{m\pi}{2l}(z + l)dz = 2\pi C_m l, \tag{13}$$

since the z-integration gives only one term, the others being equal to zero. C_m is used for the expression

$$- \sum_{\mu}\sum_{m=1}^{\infty} A_{\mu,\,m}\left[v_0 e^{-Rt_1} + \frac{B}{R}(1 - e^{-Rt_1})\right] J_0(\mu r). \tag{14}$$

We get, therefore,

$$A_{\mu,\,m}' = \frac{- 2\pi A_{\mu,\,m}\left[v_2 e^{-Rt_1} + \frac{B}{R}(1 - e^{-Rt_1})\right]\int_0^a J_0(\mu r) r\,dr}{\pi a^2 J_1^2(\mu a)}. \tag{15}$$

Putting

$$\int_0^a J_0^2(\mu a) r\,dr = \tfrac{1}{2}a^2 J_1^2(\mu a)$$

and putting this value of $A_{\mu,m}'$ as the constant of Equation (3) we have the solution for $t > t_1$ as follows:

$$\begin{aligned} V'' &= v_0 + Bt_1 - \sum_{\mu}\sum_{m=1}^{\infty} A_{\mu,\,m}\left[v_0 e^{-Rt_1} \right. \\ &\qquad \left. + \frac{B}{R}(1 - e^{-Rt_1}\right] e^{-R(t-t_1)} J_0(\mu r)\sin\frac{m\pi}{2l}(z + l). \end{aligned} \tag{16}$$

The convergence of this series is greatly helped by the fact that the terms are alternately plus and minus.

Figure 1 shows a theoretical and an experimental curve for Case II.

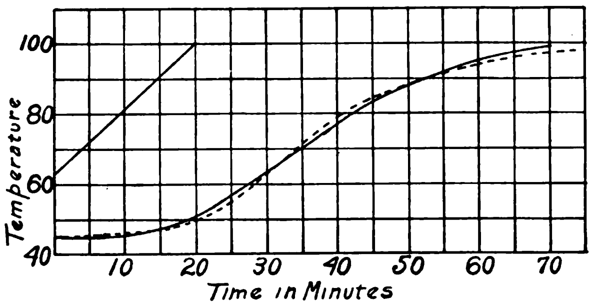

Fig. 1.

The broken line is the theoretical and the full line the experimental curve, both referring to temperatures at the center of the cylinder. The surface temperature was about 63° C. initially and increased to 100° C. in twenty minutes, remaining constant thereafter. The cylinder in this case was a pint Mason fruit jar filled with spinach as it is ordinarily canned. The agreement between the two curves is satisfactory when it is remembered that the experimental conditions approximate only roughly to the theoretical conditions. In practice the diffusivity increases with temperature while it was assumed constant in plotting the theoretical curve.

In order to show how the variations of surface temperature modify the rate of heating the curves of Fig. 2 have been plotted, using arbitrary

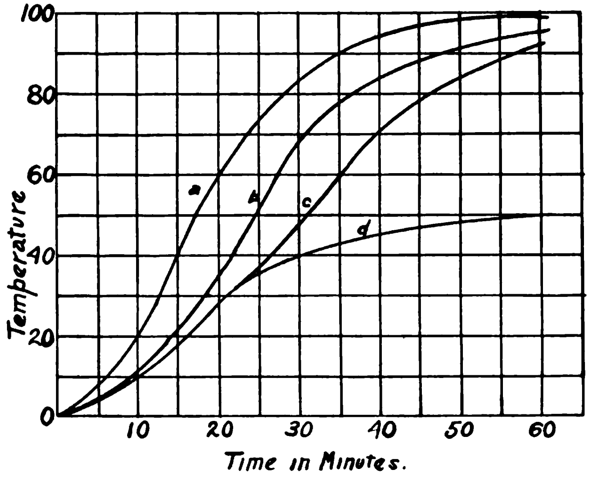

Fig. 2.

values for the constants of the equations. The curves plotted apply to the center of the cylinders only. Curve *a* is computed from Equation 3. The initial interior temperature of the cylinder is 0° C. throughout and the bath is maintained at 100° C. from the beginning. Curve *b* is computed from Equations 12 and 16. The conditions are the same as in Curve *a*, except that the surface temperature varies uniformly from 50° C. to 100° C., reaching the latter value after 20 minutes and remaining constant thereafter. Curve *c* is computed from Equations 3 and 8. The surface temperature is maintained at 50° C. for 20 minutes and then suddenly increased to 100° C. and maintained at this temperature indefinitely. Curve *d* is computed from Equation 3, the surface temperature being 50° C. continuously from the beginning.

The author desires to express his indebtedness to the late Professor James MacMahon of Ithaca, N. Y., for the solution of the equations given under Case II.

PHYSICS DEPARTMENT,
IOWA STATE COLLEGE,
AMES, IOWA,
May, 1922.

AN EXTENSION OF THE PRINCIPLE OF THE DIFFRACTION EVOLUTE, AND SOME OF ITS STRUCTURAL DETAIL.

By G. G. Becknell and John Coulson.

Synopsis.

Diffraction Patterns inside Shadows due to Point Sources of Light.—(1) *Conic section shadows.* In confirmation and continuation of the results in the preceding article, the patterns are found to depend only on the shape of the shadow, the Arago spot being obtained at the center of the circular shadow even when this was cast by a spiral edge of large pitch ground to the form of a truncated cone, when the point source was placed at the apex. Patterns inside the shadows of hyperbolic and parabolic plates were also obtained and are reproduced. As in the case of the ellipse, the predominant figure in each case is the evolute of the edge of the shadow. (2) *This general relation between diffraction caustic and shadow* is found to hold even in the case of the *shadow of the involute of a circle*, when the diffraction figure was identical with the generating circle which was, of course, the evolute of the edge of the shadow. A series of photographs of elliptical shadows show that the diffraction caustics are not continuous curves. The changes of detail and of color in the patterns with change of ellipticity of the shadow are described at some length.

In a previous paper[1] reported in this journal it was shown that for circular and ellipitcal plates illuminated by a point source, whatever the position of the plates with reference to the wave-normal, a predominant figure was produced behind the object which proved to be the evolute of the geometrical shadow.

Knowing the general mathematical relations between plane curves and their evolutes, it did not seem probable that the example there discussed of the relation between an elliptical shadow and its diffraction figure could be merely an isolated case of a curve and its evolute. This paper presents illustrations of diffraction patterns produced by parabolas, hyperbolas, and other diffracting objects.

Accurate parabolic and hyperbolic plates were produced by a lathe method similar to that discussed in our former paper for elliptical plates. In this case a cone was used instead of a cylinder. By holding thin plates of metal between proper sections of the cone it was possible to turn out both shapes at one operation. However, in the case of the parabola it was necessary that the cone be sliced well back from the apex. Otherwise, the bevelled edge of the plate caused the shadow to be that of two overlapping parabolas. It is also worth noting that it is far more difficult to turn out a true parabola than a true hyperbola since the parabolic section must be accurately parallel to the generator of the cone. Much of the success in producing these plates is due to the careful workmanship of Mr. G. S. Shallenberger, our department mechanician.

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[1] See page 594, this issue.

The apparatus and its arrangement were the same as used previously. The diffracting plates were supported on a rod extending along the axis of symmetry of the figure in such a way as not to interfere with the diffraction pattern. The plates were then oriented until the patterns were symmetrical with respect to the axis just mentioned.

Plate I., No. 1, shows the shadow and diffraction within the shadow of a hyperbolic plate whose height along the axis was 1.85 cm., and whose base was 3.6 cm. No. 2 shows the corresponding photograph for a parabola of height 2.7 cm., base 2.4 cm. The curves are precisely the ones anticipated, and measurements taken from the plates prove them to be true evolutes.

The equation of the hyperbola referred to its vertex is

$$(x/a)^2 + 2(x/a) - (y/b)^2 = 0.$$

And the equation of the corresponding evolute is

$$[a(a + x)]^{2/3} - (by)^{2/3} = (a^2 + b^2)^{2/3}.$$

In order to determine the values of a and b for the hyperbola an outline of the plate was projected upon coördinate paper and corresponding values of x and y for a number of points were recorded. The best values for the a and b corresponding to the geometrical shadow were then found by the method of least squares to be 1.26 cm. and 1.08 cm. respectively. These values show upon computation that the hyperbola and its evolute do not intersect. The photograph indicates, also, that the same is true of the diffraction figure and the outline of the shadow.

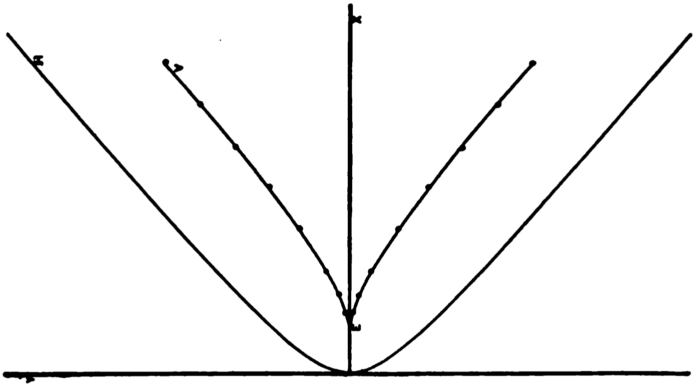

Fig. 1.

Fig. 1 shows the hyperbola and corresponding evolute computed for the geometrical shadow using the values of a and b above. The circles indicate points taken at random from the diffraction curve on the photographic plate (Plate I., No. 1).

Fig. 2 illustrates similar curves for the parabolic shadow. The equation of the evolute for the parabola $y^2 = 4ax$, is

$$y^2 = 4(x - 2a)^3/27a.$$

These curves always intersect at the point $x = 8a$, $y = 4a\sqrt{2}$. This is in agreement with the photograph (Plate I., No. 2.)

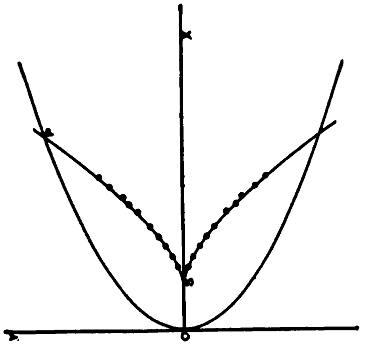

Fig. 2.

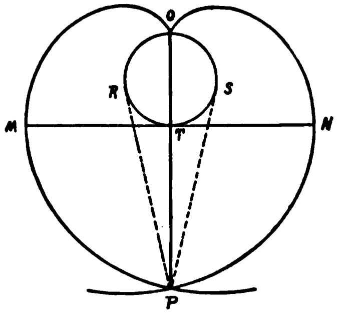

Fig. 3.

In order to apply this general principle of the diffraction evolute to other figures than conic sections a plate was cut in the form of the heart-shaped portion of the involute of a circle. This was done by unwinding a waxed thread from a small cylinder. A needle fastened to the free end of the thread was used to cut the outline of Fig. 3 from a sheet of heavy lead foil. From the construction it follows that the evolute of this curve is the original circle. Plate I., No. 3, reproduces the shadow of one of these heart-shaped plates and the diffraction figure accompanying it. The plate was about 2.5 cm. in length between the points of the heart, and was produced from a cylinder 8 mm. in diameter. The diameter of the circle as measured from the photograph agrees with that of the predicted evolute within 2 per cent.

It may be instructive to point out that there is not a one-to-one correspondence between the points of the circular evolute and those of the heart-shaped outline shown in Fig. 3. However, such correspondence does hold between the circle and the outline *MON*. This has been observed by placing a straight-edged screen over the portion *MPN* of the diffracting plate. In this case the whole circle was clearly visible. When the portion of the plate lying above *MTN* was covered the diffraction figure was only the arc *RTS*.

Examination of the photographic illustrations in this and in our preceding paper show that the shadows are crossed by a multitude of bright lines running normal to the edge. These lines are clearly developed in Plate I., No. 4, which was produced by a heart-shaped plate cut from paper, and the diffraction figure is seen to be a true envelope or caustic. From this it is probable that shadows and the diffraction patterns lying therein may be ascribed to the diffraction normals at the boundary of the shadow.

It seems, then, to be true in general *that whenever an object illuminated by a point source produces a diffraction pattern within its shadow, the predominant diffraction figure is the evolute of the geometrical shadow.*

The production of the Arago spot has always been associated with the disc or sphere as the diffracting object. However, it was shown in our first paper on this subject that an elliptical plate producing a circular shadow also has associated with it a true Arago spot. A still more striking case is furnished by a diffracting object in the form of a spiral. Plate I., No. 6, is the circular shadow and Arago spot produced by a ¾-in. (1.90 cm.) auger bit of 1-in. (2.54 cm.) pitch ground to the form of a truncated cone and illuminated by a point source at the apex of the cone (see Plate I., No. 7).

If the axis of the cone is not accurately perpendicular to the wave front the shadow cast is not strictly circular, although it may apparently be so. In such a case the diffraction figure consists of two caustics. These are illustrated in No. 8. When the cone was reversed so that the apex was turned away from the point source, no adjustment whatever was capable of producing a true Arago spot. The nearest approach to a circular spot was crescent shaped with a dark shadow on the concave side, similar to one of the caustics in No. 8. It should be observed in this instance that the geometrical shadow could never be circular. The explanation of an Arago spot produced by such a device as the one here discussed, that is, by means of a spiral object, is a decided departure from the concept of Fresnel zones.

It may be said that the experiments discussed here and in the preceding paper seem to indicate the following general principle: *Any particular form of geometrical shadow is always associated with the same diffraction pattern whatever be the diffracting object.*

THE DETAIL IN THE STRUCTURE OF THE EVOLUTES.

It seems desirable to call attention to certain peculiarities of the diffraction evolutes of the conic sections. In order to make a more minute study of the formation of the evolutes of ellipses and circles the

PHYSICAL REVIEW, SECOND SERIES, VOL. XX.
December, 1922.

PLATE I.
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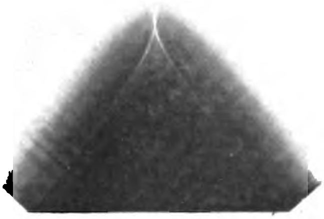
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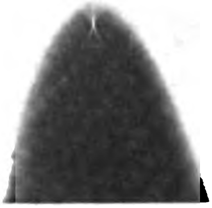
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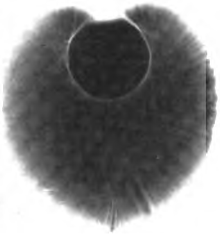
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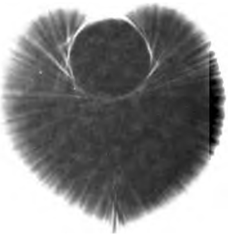
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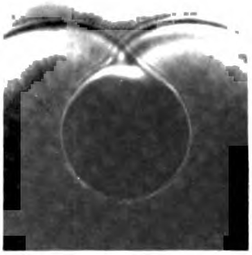
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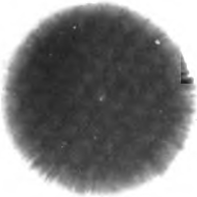
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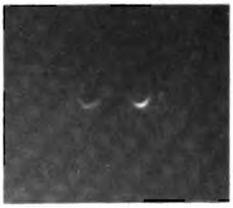
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G. G. BECKNELL AND JOHN COULSON.

distance from pinhole to photographic plate was increased from the usual distance of 7 meters to 20 meters. The diffracting plate was placed 3 meters from the pinhole instead of 2 meters. This arrangement produced about double the magnification previously used.

Plate II., No. 9, shows the diffraction pattern due to an ellipse of major diameter 1.6 cm. when placed with its plane perpendicular to the wave-normal. It will be observed that a series of bands lies *inside* the evolute and parallel thereto; and that the intensity of the bright bands diminishes rapidly as they recede from the evolute. The evolute consists of a number of separate flame-like streaks or "flares" which are merely the terminals of the bright bands within. As the eccentricity of the elliptic shadow diminishes the number of flares in a quadrant of the evolute decreases; and, therefore, likewise the number of bands within the evolute. This is illustrated by No. 10, taken for the ellipse above rotated through an angle of 25°. A similar decrease in the number of bands accompanies a reduction in the size of the plate when distances are kept constant.

A disc casting an elliptical shadow produces diffraction patterns identical with those just described when the dimensions of the shadows correspond. Plate II., Nos. 11, 12 and 13, were made with a disc .98 cm. in diameter, and correspond to angles of rotation from the normal position of 30°, 60° and 75° respectively. These illustrations bring out still more clearly the discontinuous nature of the diffraction evolute.

In the case of elliptical shadows there is always a set of bright and dark bands lying in the direction of the major axis. These become more distinct with increasing eccentricity of the shadow, as shown by Nos. 12 and 13. Similar strong bands appear in the patterns produced by an ellipse. When such a plate is rotated about its minor axis toward the position producing a circular shadow these bands gradually vanish, reappearing upon further rotation of the plate, but with an orientation in direction of 90°. That is, the direction of these bands in all cases is that of the *major axis* of the elliptical shadow.

Nos. 14, 15, 16 and 17, were taken with a carefully turned disc 5 mm. in diameter, the distance from source to photographic plate being increased to 33 meters. No. 14 shows the Arago spot and accompanying rings. Precisely the same pattern has been produced by an elliptical plate when casting a circular shadow. When the disc is rotated 20° from this position about an axis in its own plane No. 15 is produced. For angles up to 10° the transition in the pattern is almost imperceptible, but becomes more rapid beyond a rotation of 20°.

No. 16 corresponds to an angle of 30°. Here the bright spot at the center has entirely disappeared and is replaced by a black figure resembling a pair of crossed dumb-bells with white knobs faintly appearing at the ends of the bars. These knobs become brighter upon further rotation of the disc. At approximately 45° a bright spot reappears at the center of the figure with a pattern as shown in No. 17. It will be observed in the last two figures that the rings which surrounded the original Arago spot have changed decidedly in shape. In No. 16 they appear elliptical while in No. 17 they are oval. The major diameter of each figure is along the minor axis of the elliptical shadow.

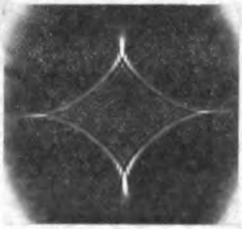
Very definite transitions in color were observed as the disc was rotated beyond the position represented by No. 15. The central spot remains white up to about 22.5°, shading into pink with increasing angle and becoming distinctly red at 27.5°. At 30° the spot has entirely disappeared. On further rotation of the disc a central spot gradually reappears, showing green at 35°, surrounded by four white spots in the form of an upright cross as in No. 16. Four distinctly red knobs appear on the crossed dumb-bells in this figure. At 45° the central dot changes to red, closely surrounded by four streaks of green, as in No. 17. At 50° the center again is black, and the four streaks have changed to white. The four flares on the axes always remain white.

Attention has been called to the fact that in the case of elliptical shadows a set of "secondary" bands lie *inside* the evolute and parallel to it, while another set extend along the major axis. The hyperbola and parabola, also, give rise to a similar series of bands. However, in Plate I., No. 3, the secondary bands occur on the *outside* of the circular evolute, and none on the inside which appears to be absolutely dark. The latter point is explained by the fact that the circular area is not traversed by any of the diffraction normals from the edge of the shadow. No. 5 shows that these secondary bands intersect at the cusp of the heart and become continuous with the usual diffraction bands lying outside the shadow.

In the case of all shadows in the form of conic sections the evolute is the envelope of the normals to the edge of the shadow which emanate from the opposite side of the axis. Thus, the areas outside the evolute are traversed by only one set of these normals; and, therefore, the secondary bands cannot exist within these areas.

UNIVERSITY OF PITTSBURGH,
July, 1922.

PHYSICAL REVIEW, SECOND SERIES, VOL. XX.
December, 1922.



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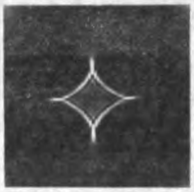

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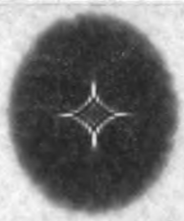

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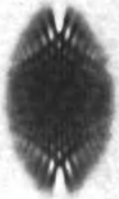

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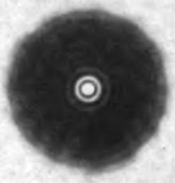

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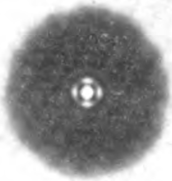

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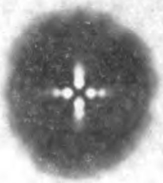

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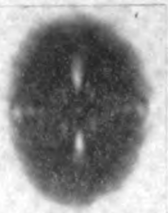

17

G. G. BECKNELL AND JOHN COULSON.

NEW EVIDENCE REGARDING THE INTERPRETATION OF CRITICAL POTENTIALS IN HYDROGEN.

By P. S. Olmstead.

Synopsis.

Critical Potentials in Hydrogen.—(1) *Experimental separation of effects due to atomic and molecular hydrogen.* In an ionization tube of the Lenard type, a close grid of tungsten wires was introduced between the filament and the gauze in front of the plate. When this grid was heated electrically to incandescence the proportion of atoms was greatly increased by dissociation of the molecules. (2) *Effects due to radiation were distinguished from effects of ionization* by comparing the electron currents to a disk electrode with those to a wire which because of its small area was relatively insensitive to effects of radiation. (3) *Six critical potentials between 10 and 16 volts* were observed and measured with reference to the strongest break, assumed to occur at 16.0 volts. Each break point was located at the intersection of two tangents; hence the relative values are probably accurate to 2 or 3 per cent. Purified electrolytic hydrogen was used. (4) *Experimental interpretation* of the breaks, which agrees in general with the previous theoretical interpretation based on quantum theory, is as follows: radiation from the atom at 10.1 and at 12.2 volts, corresponding to the first two terms of the Lyman series; ionization of the molecule at 11.5 volts and of the atom at 13.6 volts; dissociation of the molecule and radiation at 12.9 volts; finally, dissociation of the molecule and ionization of one of its parts at 16.0 volts. The energy required for dissociation of the molecule is therefore equivalent to about 2.8 volts.

Introductory.

The conclusions, which have been published by recent investigators on the critical potentials of hydrogen, were collected and tabulated in a recent paper by Professor K. T. Compton and the author.[1] Since that time, reports by Mohler, Foote, and Kurth[2] and O. S. Duffendack[3] and a paper by P. E. Boucher[4] have been added to the list of references. The effects which have been observed fall under five heads, which are noted in Table I.

Table I.

Type of Effect.	Due to	First Observed at
Radiation	Atom	10.0 to 11.0 volts
Ionization	Molecule	10.8 to 11.5 volts
Dissociation plus radiation	Molecule	12.5 to 13.9 volts
Ionization	Atom	13.1 to 14.4 volts
Dissociation plus ionization	Molecule	15.8 to 17.1 volts

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[1] K. T. Compton and P. S. Olmstead, Phys. Rev., 17, 45, 1921.

[2] Mohler, Foote and Kurth, Phys. Rev., 19, 414, 1922.

[3] O. S. Duffendack, Phys. Rev., 19, 533, 1922.

[4] P. E. Boucher. Phys. Rev., 19, 189, 1922.

Except in the work of Mohler, Foote, and Kurth and of Duffendack, the interpretations which appear in the second column of the table are the result of comparison of observed radiation and ionization potentials with the theoretical potentials based on some theory of the hydrogen molecule. The present paper deals with an *experimental separation* of the effects which are due to the atom from those which are due to the molecule.

APPARATUS. TREATING OF ITS SPECIAL FEATURES.

The apparatus used in this work was the one which was described in a previous paper[1] as one to "permit of more refined observations to test some of the considerations involved in the problem." In Fig. 1 it is seen in cross-section. It consisted of a glass tube containing the usual elements of a Lenard type of ionization tube, with the addition of a heating arrangement placed as close as possible to the gauze. At *F* was a spiral tungsten filament (seen in cross-section, end on), across which the voltage drop was 1.6 to 1.7 volts for a current of 3.5 to 4.0 amperes. The spiral consisted of three turns only, in the middle of the filament. Since this part of the filament was hotter than the rest, and since the potential drop across the spiral part was but a small fraction of a volt, the filament was practically an equipotential source of electrons. At *G* was a gauze covering one end of a platinum cylinder, which was connected with the galvanometer by a lead through a side-tube *L*, in order to measure the total electron emission from the filament. As close as possible to the gauze and between it and the filament, was a heating grid, consisting of twenty fine tungsten wires *TT* strung between two copper plates *HH* so that the wires of the grid were perpendicular to the filament.

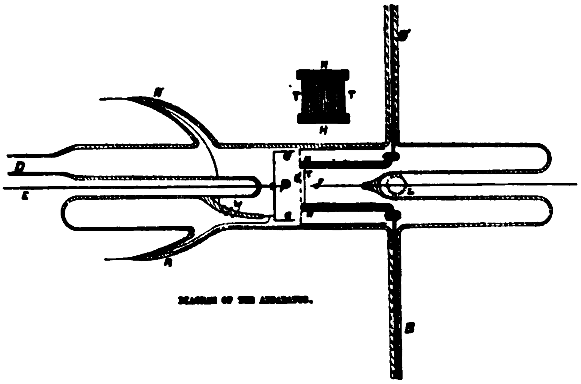

Fig. 1.

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[1] Loc. cit.

The copper plates were insulated from the gauze and its supporting cylinder by small quartz blocks. The electrical connections to the grid were made by means of heavy copper wires to the plates sealed through the long glass tubes BB^1 with De Khotinsky cement at their ends. It was necessary to keep these tubes very cool to prevent the cement from melting due to the heat conducted along the wires. The second special feature of the apparatus was the receiving electrode or plate. This consisted of two parts—a single platinum wire P of small cross-sectional area, and a platinum cup C which surrounded P and could either be joined to P or insulated from it. When joined and connected to the electrometer the combined effect of radiation and ionization was observed, while if P alone were connected to the electrometer, ionization only was measured, since the area of P was too small to intercept enough radiation to give an appreciable photoelectric effect. Suitable guard rings were placed at strategic points to prevent leakage to the electrometer. One of these is shown at W. At D was a connection to the diffusion pump, McLeod gauge, and source of hydrogen. Between them and the tube were two liquid air traps, the one nearest the tube being filled with coconut charcoal.

The hydrogen was obtained as in the previous work by the electrolysis of sulphuric acid. The processes involved in purifying the gas are explained in the previous paper. The tube was "baked out" by heating in a furnace to about 300° C., keeping the tube pumped out at the same time. It was further cleansed of the unwelcome residual gas by "washing out" with hydrogen, the hydrogen being introduced and pumped out at various times during the baking.

The tungsten grid TT, placed as close to the region of effective electron impacts as possible without introducing disturbing effects from positive thermions, served to vary the proportion of dissociated, or atomic, hydrogen.[1] Any effect which was relatively enhanced by raising the grid to a high temperature must be due to atomic hydrogen. Similarly, any effect which was relatively more pronounced when detected by the point P than by the cup C was attributed to ionization.

The method of obtaining the experimental readings was such as to give the greatest relative accuracy. Under the same conditions of gas pressure and current flow in the gas, as observed in the galvanometer deflections, it was possible to duplicate the values of the electrometer readings at specified accelerating voltages to within two or three per cent. in different runs, even in the region of greatest variation of the electrometer readings with the accelerating voltage, *i.e.*, in the region from

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[1] Langmuir, Jour. Amer. Chem. Soc., 37, 417, 1915.

15 to 16 volts. In fact the individual curves from which the "Grid off for Radiation" average curve (Fig. 2) was obtained differed from the average by less than one per cent.

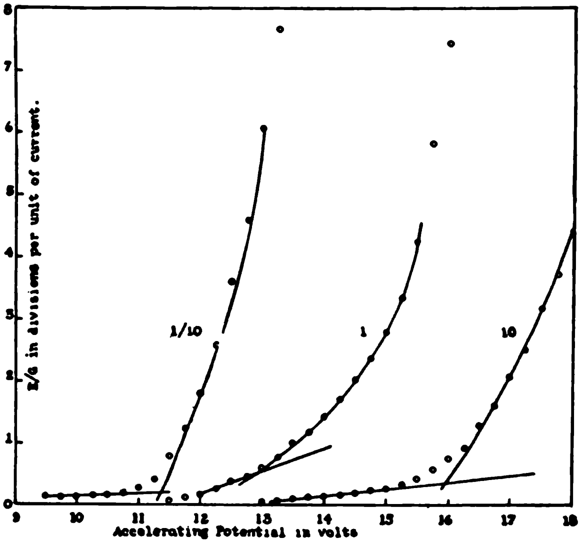

Fig. 2.

"Grid off for Radiation" Curve Breaks: 11.4; 12.9; 16.0.

EXPERIMENTAL RESULTS.

In this tube are two totally independent elements which may be varied independently, and hence we expect to find four types of experimental results. First, we may connect only the platinum point *P* to the electrometer, and have the grid on. Curves obtained with this set-up are called "Grid on for Ionization" curves and will be denoted by *I* (on). Next, we may keep the electrometer connections the same but turn the grid off. This gives a set of "Grid off for Ionization" curves and they will be denoted by *I* (off). The two other possibilities are obtained by connecting the cup *C* as well as the point *P* to the electrometer, giving the arrangement suitable for observing the combined effect of radiation and ionization. We then get the sets of curves—"Grid on for Radiation," *R* (on), and "Grid off for Radiation," *R* (off). These four types of curves are illustrated by the average curves (Figs. 2, 3, 4 and 5), each of which is the average of a number of independent runs. These curves have been corrected from the observed relations by adjusting the accelerating voltage on each of the original curves so that the big "break," which corresponds to dissociation of the molecule plus ionization of one of its parts, may come at 16.0 volts. The adjustment was an empirical one which made the line representing the slope of the curve after passing the break point cut the line representing the slope of the curve before reaching the break point. Since this intersection depends largely on the way in which the intersecting lines are chosen, the plots were consistently made so that the line on either side of the break point was fairly straight for a region of two volts. Velocity distribution curves were not generally taken, since the object of this work was to find the peculiarities of the lower breaks and to locate their positions relative to the large breaks.

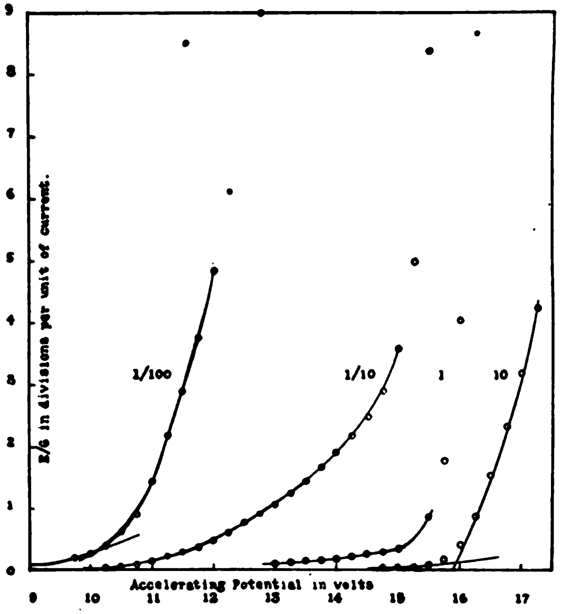

Fig. 3.

"Grid off for Ionization" Curve Breaks: 10.1; 11.5; 16.0.

In order to obtain a convenient comparison between the different effects, four ratio curves were computed. These are based on the four average curves typifying the four sets of experimental results. Each of these average curves shows the average of several experimental curves which were taken under approximately similar conditions of pressure of hydrogen, and, to a certain extent, of electron current as given by the galvanometer readings. With regard to this it was found that, if the pressure and accelerating voltage were kept constant, the ratio of the electrometer reading to the galvanometer reading E/G would be approximately constant. Thus in all these results it is this ratio, or the electrometer deflection per unit bombarding current of electrons, which

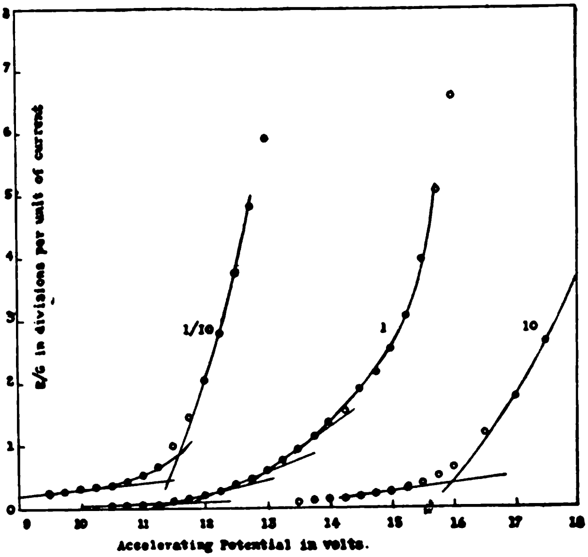

Fig. 4.

"Grid on for Radiation" Curve Breaks: 10.2; 11.4; 12.2; 12.9; 13.7; 16.0.

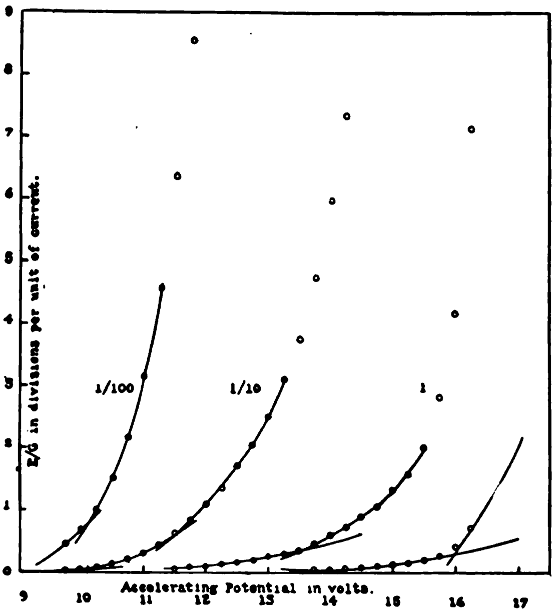

Fig. 5.

"Grid on for Ionization" Curve Breaks: 10.1; 11.5; 13.6; 16.0.

has been plotted against the accelerating voltage. Then from these curves were obtained the ratio curves:

$$\frac{I\ (\text{on})}{I\ (\text{off})}, \quad \frac{R\ (\text{on})}{R\ (\text{off})}, \quad \frac{R\ (\text{on})}{I\ (\text{on})}, \quad \frac{R\ (\text{off})}{I\ (\text{off})}.$$

These are shown in Figs. 6, 7, 8 and 9. The values for the points for these ratio curves were obtained from the calculated values of the averages rather than by reading the curves, so that the ratio curves themselves are experimental curves and have not been smoothed by smoothing the average curves in any way.

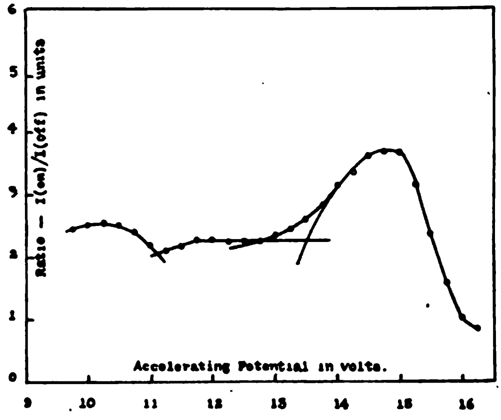

Fig. 6.

Ratio Curve for *I* (on)/*I* (off).

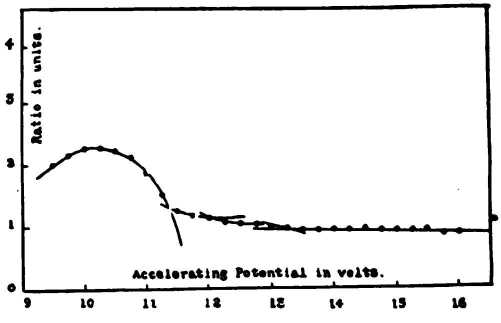

Fig. 7.

Ratio Curve for *R* (on)/*R* (off).

Discussion of Results.

The interpretation of these results will be considerably facilitated if first a careful study is made of the way in which the individual ratio curves should behave. Take, for instance, the ratio *I* (on)/*I* (off), Fig. 6. With the grid on we should get a greater concentration of atomic hydrogen; hence when this ratio is greater than unity it means that the effect due to the atom has been increased relative to that due to the molecule. Thus, any effect which tends to bend the ratio curve toward the unity line would be interpreted as an increase in an effect due to the molecule while anything which turns the slope away from the unity line would be taken as due to the atom. The same thing may be said of the ratio *R* (on)/*R* (off), Fig. 7. Now let us consider the conclusions which may be drawn

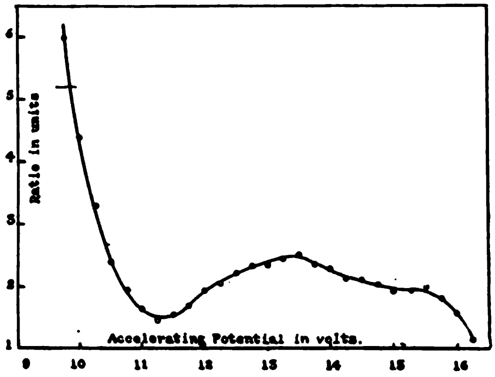

Fig. 8.

Ratio Curve for *R* (on)/*I* (on).

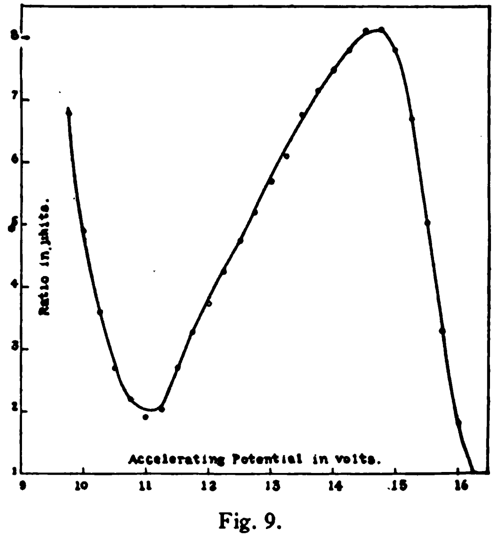

Fig. 9.

Ratio Curve for *R* (off)/*I* (off).

from the two curves. If the ionization curves should show the increased effect due to the hot grid, but the radiation curves should not, the effect itself would be taken as ionization and also as due to the atom. In like manner it is possible to get further differentiations of ionization and radiation.

Table II.

Data Obtained from the Ratio Curves.

Range of the Effect (Volts).	Interpretation.	Reason.
9.50 to 10.2...	Radiation from atom	$\frac{R\ (\text{on})}{I\ (\text{on})}$ and $\frac{R\ (\text{off})}{I\ (\text{off})}$ both start high. $\frac{R\ (\text{on})}{R\ (\text{off})}$ curve starts high and increases.
10.2 to 11.4....	Ionization due to molecule	Both $\frac{R}{I}$ curves decrease sharply. Effect is not increased by grid on.
11.4 to 12.1....	Radiation from atom	Strong increase in $\frac{R}{I}$ curves. Upward tendency in $\frac{R\ (\text{on})}{R\ (\text{off})}$ curve.
12.1 to 13.0....	Radiation from molecule	$\frac{R}{I}$ curves show no falling off. $\frac{R\ (\text{on})}{R\ (\text{off})}$ curve slightly deflected downward.
13.0 to 15.0....	Ionization due to atom	$\frac{R\ (\text{on})}{I\ (\text{on})}$ curve strongly flattened. $\frac{R\ (\text{off})}{I\ (\text{off})}$ curve practically unaffected. $\frac{I\ (\text{on})}{I\ (\text{off})}$ curve increases strongly. $\frac{R\ (\text{on})}{R\ (\text{off})}$ curve very slightly inflected upward.
15.0 to limit of investigation.	Ionization due to molecule	Strong decrease in $\frac{R}{I}$ curves. No increase in $\frac{R\ (\text{on})}{R\ (\text{off})}$ curve. Strong decrease in $\frac{I\ (\text{on})}{I\ (\text{off})}$ curve.

The other two ratio curves also have certain peculiarities. The grid remains unchanged while the type of effect is varied. If the radiation effect is large relative to the ionization effect, the curve will be greater than unity, whereas if the effect is mainly ionization the curve will tend to remain near unity. Those effects which tend to bend the curve away from the unity line are due to radiation and those which tend to bend it toward the unity line are due to ionization.

Considered with this interpretation of their behavior, these four curves make it possible to construct Table II. This shows the whole field of the investigation blocked off into units, and gives the type of effect that is most important in each unit. It remains to indicate the way in which these units are consistent with the breaks that appear on the experimental curves (Figs. 2, 3, 4 and 5). As in the case of the ratio curves we will first consider what may be expected to happen in each of these average curves. With the grid off we should not expect effects due to the atoms, but on the other hand effects due to molecules would be very sharp. Thus on the "Grid off for Ionization" curve only ionization from molecules should be observed. Similarly, on the "Grid off for Radiation" curve we should observe radiation and ionization from the molecules only. On the other hand the curves with the grid on should give both the molecular and atomic effects. The "Grid on for Radiation" curve should give all the breaks and the "Grid on for Ionization" curve all the ionization but none of the radiation effects. Accordingly, if we turn to the curves themselves, we may classify our results as shown in Table III. We note that, except for the last item, just the effects expected according to the above analysis are observed. We are therefore compelled to ask the question, "Why do we get an effect due to radiation

TABLE III.

Breaks Observed on the Experimental Curves.

Position.	Observed at (Volts)	Interpretation.	Curve.
16.0.....	16.0	Dissociation of molecule plus ionization of one atom	"Grid on for Ionization"
	16.0		"Grid off for Ionization"
	16.0		"Grid on for Radiation"
	16.0		"Grid off for Radiation"
13.6.....	13.6	Ionization of atom	"Grid on for Ionization"
	13.7		"Grid on for Radiation"
12.9.....	12.9	Dissociation of molecule plus radiation from one atom	"Grid on for Radiation"
	12.9		"Grid off for Radiation"
12.2.....	12.2	Radiation from atom	"Grid on for Radiation"
11.5.....	11.5	Ionization of molecule	"Grid on for Ionization"
	11.5		"Grid off for Ionization"
	11.4		"Grid on for Radiation"
	11.4		"Grid off for Radiation"
10.1.....	10.1	Radiation from atom	"Grid on for Ionization"
	10.1		"Grid off for Ionization"
	10.2		"Grid on for Radiation"

from the atom in three sets of curves when we expect it only in one?" This is easily answered when the electrical connections which were used for ionization and for radiation are considered. It is seen that in the "Grid off for Radiation" curve the effect is not observed, which is as expected. With the connections for ionization, however, there is a larger volume of gas in which the effective collisions take place and, since no ionization of any kind was detected below 11.5 volts, any small effect before that must be due to radiation. To account for a certain amount of atomic effect present even when the grid is off we turn to the filament itself. This is very hot, and besides giving off electrons, is able to decompose a certain amount of the gas near it. Whatever effect is present in the region of 10 to 11 volts would be more noticeable than any effect of the same order of magnitude farther up in the curve where it would be superimposed on another effect of a much larger magnitude. For this reason it is possible to detect the radiation from the 10.1 volt effect even with the point P alone as the detecting electrode.

In discussing these curves we should not overlook the characteristics of the breaks. We note that the break at 16.0 volts is not as sharp nor as distinct as the others but seems to start a volt or more before the steep rise in the curve takes place. We note that the other breaks are singularly distinct, so that it is usually possible to draw smooth curves on either side of the break so that they either pass through all the observed points or at most neglect one or two. The obvious explanation of this difference is that it is due to the fact that all the electrons emitted by the filament do not have the same velocity, so that it is possible for some of the electrons to have the velocity required to produce the observed effect with a smaller accelerating potential than others. For this reason we need a sliding scale to determine at what true voltage the various effects set in.

Suppose that P_m is the probability of an electron striking a molecule of gas; P_a the probability of striking an atom of the gas; and p the probability of an electron being emitted from the filament with a velocity sufficient to produce the desired effect. P_m will be proportional to the number of molecules in a unit volume of the gas and therefore is practically proportional to its pressure, since the partial pressure of the atoms is always small. In like manner the value of P_a will be proportional to the number of atoms in the gas. We know that there is always a relationship between the number of atoms and molecules which remain in equilibrium at any temperature. This relationship depends on thermodynamical considerations. If we supply energy to the gas we can keep a larger proportion of the particles in the atomic form. In this work this was made possible by the introduction of the heating grid. Even when the grid is off a certain amount of atomic hydrogen will be in the tube due to dissociation by the filament itself. This, of course, is not formed at the place where it is most effective and thus it will be observed only when the other effects are almost negligible in comparison. To take a numerical analogy to the situation here, suppose that there were in the case with the grid off 99 molecules to every 1 atom. Then the observed effects due to the molecule would be 99 times as strong as that due to the atom. Then let us suppose that with the grid on we have 90 molecules to every 10 atoms. Now the effect due to the molecule is only 9 times that due to the atom, but we have also changed two other factors. The effect due to the atom has been increased 10 times and the effect due to the molecule has been slightly decreased, but has practically the same value as before. Thus we see we can express the probability of striking an atom in terms of the probability of striking a molecule as

$$P_a = kP_m,$$

where k is a constant depending on the linear relation of the number of atoms to the number of molecules, or in this particular case on the amount of dissociation produced by the grid. But, in addition to striking a molecule or atom, we must have a transfer of energy at the collision in order to produce the desired effect. If the electron making the collision does not have sufficient energy to produce the effect, the energy cannot be transferred. On the other hand, if the electron has more, it can, of course, give it. We know that the energy of an electron is proportional to the square of its velocity, so if we assume Maxwell's Law of Distribution of Velocities we can get an idea of the probability of having a particular velocity or more, and in so doing get a corresponding probability of having a specified amount of energy or more. This is a more difficult thing to consider. In Table IV. is given, against tenths of the mean energy, the percentage of electrons having less than the specified part of the mean energy (F), the percentage of electrons having more than the specified part of the mean energy ($1 - F$), the percentage of electrons having energies in the interval between two successive specified divisions of the energies (dF), and the mean energy of all electrons having energy greater than the amount specified in the first column. This is expressed in terms of the mean energy of all the electrons and in equivalent volts. Thus, to take a specific example, 50.64 per cent. of the electrons have less than 0.8 times the mean energy, 49.36 per cent. have more, and the mean energy of these 49.36 per cent. is 1.61 times the mean energy of all the electrons, or 0.97 volt. The expression in equivalent volts is obtained from the average correction for a filament temperature of 2350° to 2400° K. This has been found to be 0.60 volt.[1] The values given in the last two columns were obtained by mechanical integration, the steps used being those tabulated.

TABLE IV.

No. of Times Mean Energy.	F.	1 − F.	dF.	Mean Energy of Group (1 − F).	
Times $\bar{E}$.	%	%	%	Times $\bar{E}$.	Volts.
0.0	0.00	100.00		1.00	0.60
0.1	3.99	96.01	3.99	1.04	0.62
0.2	10.35	89.65	6.36	1.10	0.66
0.3	17.46	82.54	7.11	1.18	0.71
0.4	24.70	75.30	7.24	1.26	0.76
0.5	31.77	68.23	7.07	1.34	0.81
0.6	38.51	61.49	6.74	1.43	0.86
0.7	44.81	55.19	6.30	1.52	0.91
0.8	50.64	49.36	5.83	1.61	0.97
0.9	55.97	44.03	5.33	1.70	1.02
1.0	60.84	39.16	4.87	1.79	1.07
1.1	65.24	34.76	4.40	1.89	1.13
1.2	69.22	30.78	3.98	1.98	1.19
1.3	72.75	27.25	3.53	2.08	1.25
1.4	75.93	24.07	3.18	2.18	1.31
1.5	78.77	21.23	2.84	2.27	1.36
1.6	81.30	18.70	2.53	2.37	1.42
1.7	83.54	16.46	2.24	2.46	1.48
1.8	85.53	14.47	1.99	2.56	1.54
1.9	87.28	12.72	1.75	2.66	1.60
2.0	88.84	11.16	1.56	2.76	1.66
2.2	91.42	8.58	2.58	2.96	1.78
2.4	93.48	6.52	2.06	3.18	1.91
2.6	94.96	5.04	1.48	3.41	2.05
2.8	96.16	3.84	1.20	3.63	2.18
3.0	97.07	2.93	.91	3.85	2.31
3.5	98.52	1.48	1.45	4.44	2.66
4.0	99.26	.74	.74	5.12	3.07
5.0	99.72	.28	.46	6.15	3.69
6.0	99.88	.12	.16	7.00	4.20

Applying this to the curves that we have obtained, we get the information given in Tables V. and VI. Here we have assumed that at the 16.0-

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[1] Sih Ling Ting, Roy. Soc. Proc., 98, 374, 1921.

volt break we can express the magnitude of the new effect coming in as a function of the number of electrons with sufficient energy to produce the effect. If no new effect were coming in, the curve would continue to increase smoothly and, supposedly, would tend to flatten out, but the new effect starts the curve upward again. In the early part of the curve this effect is due only to a few of the electrons, but, with increasing voltage, more are able to produce the effect. It is assumed that in this interval of about a volt or a volt and a half the major part of the difference between the extrapolated curve and the observed curve is due to the distribution of velocities. To obtain a significant quantity the difference between the observed and extrapolated curves was divided by the percentage of electrons with total energy sufficient to take part in producing the effect. If we are correct in assuming that all electrons with energies greater than 16 volts are equally likely to produce ionization at impact (which is probably nearly true in the small range of velocities

TABLE V.

Accel. Poten., Volts.	Correction.		Per Cent. having this Correction.	Grid off for Radiation.				Grid on for Radiation.			
	Volts.	$\bar{E}$.		Reading.	Extr. Curve.	Difference.	$\frac{\textit{Diff.}}{\%}$.	Reading.	Extr. Curve.	Difference.	$\frac{\textit{Diff.}}{\%}$.
15.00	1.75	2.92	2.8	2.8	2.8	0.0	0.00	2.5	2.5	0	.00
15.25	1.50	2.50	4.5	3.3	3.2	0.1	0.02	3.1	2.9	0.2	.05
15.50	1.25	2.09	7.5	4.2	3.6	0.6	0.08	4.0	3.1	0.9	.12
15.75	1.00	1.67	12.7	5.8	4.0	1.8	0.14	5.1	3.4	1.7	.13
16.00	0.75	1.25	21.5	7.4	4.4	3.0	0.14	6.6	3.8	2.8	.13
16.25	0.50	0.84	37	9.2	4.8	4.4	0.12	8.6	4.1	4.5	.12
16.50	0.25	0.42	62	12.9	5.2	7.7	0.12	11.9	4.5	7.4	.12
16.75	0.00	0.00	100	16.1	5.6	10.5	0.11	14.5	4.8	9.7	.10

TABLE VI.

Accel. Poten. Volts.	Correction.		Per Cent. Having this Correct.	$(\%)^{3/2}$.	Grid off for Ionization.				Grid on for Ionization.			
	Volts.	$\bar{E}$.			Reading.	Extr. Curve.	Difference.	$\frac{\textit{Diff.}}{(\%)^{3/2}}$.	Read.	Extr. Curve.	Difference.	$\frac{\textit{Diff.}}{(\%)^{3/2}}$
15.00	1.75	2.92	2.8	4.7	0.4	0.4	0.0	0.000	1.3	1.3	0.0	0.000
15.25	1.50	2.50	4.5	9.6	0.5	0.4	0.1	0.010	1.6	1.4	0.2	0.022
15.50	1.25	2.09	7.5	20.6	0.9	0.4	0.5	0.024	2.0	1.6	0.4	0.019
15.75	1.00	1.67	12.7	45.6	1.8	0.4	1.4	0.031	2.8	1.8	1.0	0.022
16.00	0.75	1.25	21.5	100	4.1	0.5	3.6	0.036	4.2	2.0	2.2	0.022
16.25	0.50	0.84	37	227	8.7	0.5	8.2	0.036	7.1	2.1	5.0	0.022
16.50	0.25	0.42	62	490	15.2	0.5	14.7	0.030	—	—	—	—
16.75	0.00	0.00	100	1,000	23.2	0.6	22.6	0.023	—	—	—	—

considered) then this ratio should be constant. For the radiation curves as given in Table V. we see that the constancy of the ratio is well established from 15.75 to 16.50, a region about one volt in length. This is about as much as can be expected. In these calculations, though provision is made for the increasing effect of the new break, we have not made the further correction in the falling off of the old break. If this is done Tables V. and VI. are changed to Table VII. In Table VI. we note that in order to obtain even an approximation to linearity the three-halves power of the per cent. must be used. This only goes to show that conditions in the tube are different in the two types of effect. It may well be that when a charged nucleus is accelerated only in the direction of emission of the electrons the effects due to it are linear but when it is forced to move in a curved path it obeys a different law. This is the case in the present problem. When the connections are arranged for observing radiation and ionization together, the charged molecules or atoms move on toward the plate in straight lines. On the other hand, in the arrangement to observe only ionization these particles are accelerated in a direction different from that in which they were moving. For this reason they will be traveling in orbits which will approximate parabolas with the wire point as their foci. Only in the case when the attraction is sufficiently great to bring the orbit within the small region occupied by the wire will the effect of the charged particle in the orbit be recorded. Another factor tending to increase the effect in the ionization curves is that more molecules and atoms may participate in collisions which will give observable effects. This is illustrated in Figs. 10 and 11. In Fig. 10, all the collisions must take place in the neighborhood of the gauze while in Fig. 11, the collisions may take place in the whole region surrounded by the gauze and cup which are kept at the same potential. We find by a study of the results that the effect is increased so that it varies with the three-halves power of the accelerating voltage.

TABLE VII.

Accel. Poten. Volts.	*R* (off) $\frac{\text{Diff.}}{\%}$.	*R* (on) $\frac{\text{Diff.}}{\%}$.	*I* (off) $\frac{\text{Diff.}}{(\%)^{3/2}}$.	*I* (on) $\frac{\text{Diff.}}{(\%)^{3/2}}$.
15.00	0.03	0.03	0.000	0.000
15.25	0.07	0.07	0.010	0.031
15.50	0.12	0.15	0.024	0.029
15.75	0.18	0.17	0.033	0.026
16.00	0.18	0.17	0.038	0.026
16.25	0.17	0.16	0.037	0.026
16.50	0.18	0.16	0.031	——
16.75	0.16	0.15	0.023	——

Up to this point the question of the determination of the position of the break point has been based on an arbitrary assumption that the curve assumes a more or less linear character both before and after the break point. Nothing has been mentioned to indicate whether this type of determination of the break should be more or less accurate than the usual one of taking the point of rise in the curve as the real break point. It has just been shown, however, that the curve has a roundness at the break point providing the break is so pronounced that the effect of the distribution of velocities becomes an important factor. If we consider the weaker breaks, which do not have this large distribution of velocity factor, we find that the curve on the two sides of the break is almost given by straight lines which are inclined to each other at a small angle. This means that if we were able to obtain a more accurate set of values near this point and could plot them on a larger scale we would find a similar distribution of velocity curve. Conversely, if we should plot on a much smaller scale the curve near the stronger breaks, where we observe the distribution of velocity correction, we would find that the limit of the curve would be two straight lines intersecting at the break point. This is the real significance of this criterion for a break. It actually makes the position of the break independent of whether the effect observed is large or small. Now concerning the accuracy with which the break is fixed, we must again consider these two types of effect. The large effects are sometimes so large that the scale must change at least once in passing through the break point. This means that we must use care in selecting the particular curve which gives the correct break point. Obviously the only one to use is the one to a scale which can show the curve for at least one or two volts on either side of the break point. The intersection of the tangents which most nearly express the remaining portion of the curve on either side of the break then gives the correct break point. We find that this gives a probable error of about .2 volt in almost every case. Thus we obtain all breaks properly spaced

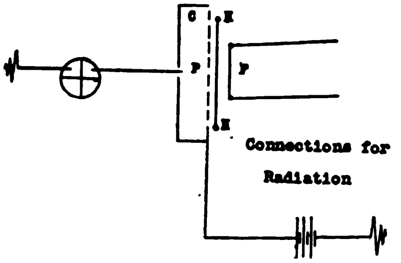

Fig. 10.

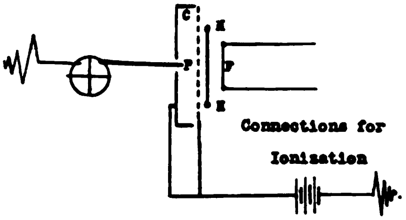

Fig. 11.

relatively to each other, independent of the velocity distribution, if we determine the position of each when plotted to a scale giving a difference of slope on each side of the break which is the same for all.

We must also try to determine the absolute accuracies of the points of discontinuity of each curve. Turning to the spectroscopic evidence we note that the 10.1-volt and the 13.5-volt breaks can be accurately computed while the breaks which are due to the molecule do not have this additional check. We have already shown that the accuracy of the big break is ± .2 volt, so we can easily compare the points at which the breaks occur and then discuss the accuracy of the positions. If we compare the values for the small breaks with the values predicted on the Bohr Theory and find how they are fixed relative to each other we find that the agreement is extremely good. So we are left with only one break to fix and we have one bit of evidence that helps us to fix that relatively to the others. Among the small breaks is the one for "dissociation of the molecule plus radiation from an atom." This was found to be 2.8 volts higher than "radiation from the atom." This 2.8 volts is therefore the energy required for dissociation of the molecule. That means that in order to fix the value for "dissociation of the molecule plus ionization from one atom" we must have from the figures which are given 13.6 + 2.8 or 16.4 volts. The result obtained was 16.0 ± .2 volts so that the values check with a maximum accuracy of .2 volt, or to a minimum accuracy of .6 volt. The most probable tendency is to place the big break too soon, for the observer is always anxious to note the beginning of an effect though it might be better for him to determine the point at which the full effect comes in rather than any intermediate point. In this case we might suppose that the small breaks were observed only when the velocity of all electrons was sufficient to give the observed effect. This would correspond, in the case of the big break, to the point at which the intermediate curve had a slope corresponding to the slope of the curve beyond the break. This adds about .5 volt to the previous observed value, giving us 16.5 as a better position of the break. This seems to agree a bit better with the other calculation. However, these suggestions are such as to show that the results are in good agreement and are really not sufficient to definitely settle the exact position of the big break. Probably this last correction, which brings the value up to 16.5 volts, is in reality too much and the actual position is somewhere between 16.0 and 16.5 volts. This seems the only logical conclusion at which we can safely arrive.

CONCLUSION.

As a result of this research, Bohr's Theory of the Hydrogen Atom has been experimentally closely verified, since both the first and second radiation potentials, corresponding to the first two terms of the Lyman Series, have been obtained. In addition it has been conclusively shown that two ionizing potentials of the molecule exist, the first at 11.5 volts leaving the molecule positively charged, while the second at 16.0–16.5 volts dissociates the molecule and ionizes one of its parts.

In conclusion, the writer wishes to express his sincere thanks to Professor K. T. Compton for his suggestions and assistance in carrying out the investigation.

PALMER PHYSICAL LABORATORY,
PRINCETON UNIVERSITY,
June, 1922.

Note: Fig. 10 should show the point *P* and the cup *C* electrically connected and insulated from the gauze.

POSITIVE-RAY ANALYSIS OF POTASSIUM, CALCIUM AND ZINC.

By A. J. Dempster.

Synopsis.

Isotopes of potassium, calcium and zinc have been determined by positive-ray analysis, using the apparatus and method previously described in which the charge deflected by a constant magnetic field through a fixed slit into a Faraday cylinder is measured as a function of the voltage accelerating the rays. Curves showing maxima corresponding to the various isotopes are reproduced. With potassium, isotopes with atomic weights 39 and 41 were found as previously observed by Aston. With pure calcium isotopes at 40 and 44, and with zinc isotopes at 64, 66, 68, and 70 were observed. After a disturbing effect of the electric field was eliminated, the ratio of the intensities obtained, 18 to 1 for the two isotopes of potassium and 70 to 1 for those of calcium, gave average atomic weights agreeing well with accepted values, 39.10 and 40.07 respectively. It is pointed out that when the determination of the relative proportions of all the isotopes of an element is made sufficiently accurate and reliable, a comparison between calculated and observed average atomic weights would give a measure of the packing effect or divergence of the weights of the isotopes from integral values. If the width of the slit used in limiting the beam of canal rays were reduced from 0.37 to .07 mm., isotopes of elements of atomic weight 100 or more should be resolved with the present apparatus.

In the following paper the method of positive-ray analysis previously described is extended to the elements potassium, calcium and zinc. The analyzing apparatus is shown in Fig. 1 and is described in detail in two previous papers.[1] The charged atoms are formed at the right and the masses for different elements may be compared by observing the total potentials applied when they are bent so as to fall on the second slit S_2. The only alteration made in the apparatus has been to cover both sides of the slit in P with fine wires a short distance apart in order to insure that the discharge is not influenced when the electric field between P and S_1 is changed.

Experiments with Potassium (Atomic Weight 39.10).

Rays of potassium were observed from two sources. They were first found associated with sodium in some preliminary attempts to obtain rays from metals with high melting points, probably from the decomposition of water glass used in the cement on the hot anode. Two components, one much stronger than the other, were readily observed two units apart in atomic weight. A comparison with sodium located the main potassium component as close to 39. The curve in Fig. 2 shows the intensity of the rays observed as the accelerating potential was altered to bring the various parts of the bundle on to the second slit.

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[1] A. J. Dempster, Physical Review, 11, p. 316, 1918; Phys. Rev., 18, p. 415, 1921.

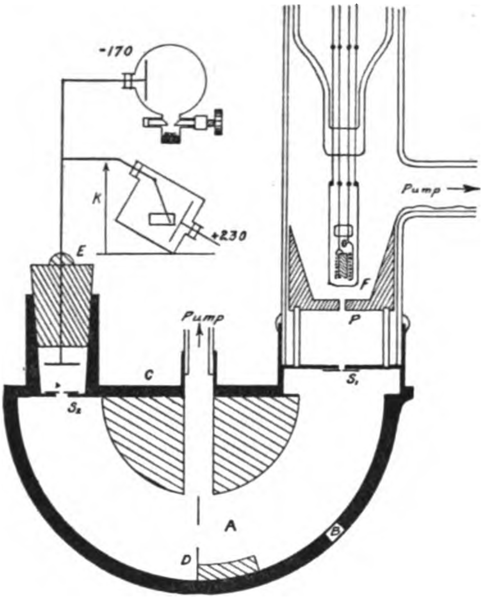

Fig. 1.

The maximum of the strong component is placed exactly at 39, and the atomic weight abscissæ are obtained by dividing 39 times 911 by the potential in volts for each measurement. The current scale for the

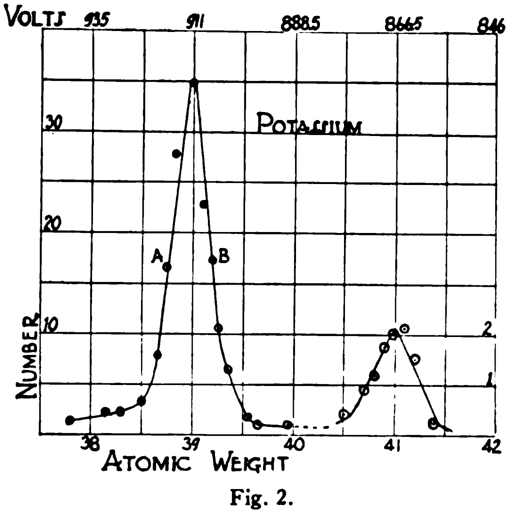

Fig. 2.

fainter isotope in the figure is made five times that for the stronger. The intensity ratio is approximately 18 to 1, giving a mean atomic mass of 39.10 in agreement with the chemical atomic weight. A possible significance of this agreement will be discussed below in connection with the measurements with calcium. Potassium rays were also measured from an anode of lithium, containing potassium as an impurity, which was heated in an iron capsule. The same two components were observed as in the case described above. The experiments thus confirm the existence of the two isotopes in potassium found by Aston with his method of analysis.[1]

Experiments with Calcium (Atomic Weight 40.07).

Calcium metal was found to be very suitable for use in this method of analysis. It was heated in an iron container and evaporated readily at a red heat. A strong line appeared suddenly as the evaporation commenced and was always accompanied by a faint line four units greater in atomic weight. The atomic weight 40 for the strong component was confirmed to 0.3 per cent. by comparison with a potassium line at 39 which appeared for a short time during the heating. Complete curves were drawn for the calcium lines, but as they are practically identical in form and sharpness with those in Fig. 2, they are not reproduced. The atomic masses of the two lines from calcium were compared by observing the potentials for the maxima. In Fig. 3 is shown the

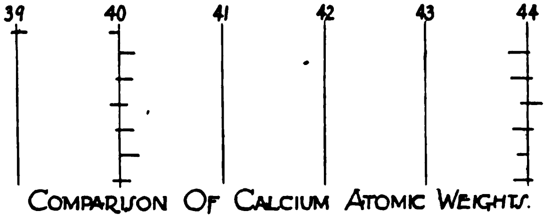

Fig. 3.

accuracy with which the observations of the maxima may be made. The center of each short line indicates the value taken as the maximum and the length of the line indicates on the atomic weight scale the estimated possible error in the setting (corresponding usually to ± 2 volts). The first two lines show the comparison with the potassium line at 39. It is seen that to the accuracy obtained the atomic weights agree with 40 and 44. With the parabola method of analysis, G. P. Thomson[2] has examined calcium rays from calcium fluoride and detected a rather broad line around 40 in atomic weight. No isotope at 44 was observed.

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[1] Phil. Mag., 42, p. 857, 1921.

[2] Phil. Mag., 42, p. 857, 1921.

The calcium used was, however, found to contain traces of calcium carbonate as an impurity, so that the rays with mass 44 might be due to carbon dioxide liberated by the decomposition of the carbonate. To avoid this uncertainty a sample of calcium was prepared by distillation in a high vacuum. Considerable quantities of gas were set free during the evaporation and continually removed by a mercury vapor pump. The calcium was condensed directly in the anode and this was then transferred to the analyzing apparatus as rapidly as possible. With the calcium thus prepared it was found that the component at 44 was still present, and was approximately 1/70 as strong as the main component. We may therefore conclude that calcium consists of two isotopes with atomic weights 40 and 44.

With the crude metal several measurements at low temperatures gave about 70 to 1 for the intensity ratio of the components, the same as found for the distilled calcium, but on increasing the temperature of the anode the component at 44 became much stronger than at low temperatures, probably due to carbon dioxide being evolved at the higher temperatures. The ratio 70 to 1 gives a mean atomic weight of 40.055, whereas the chemical atomic weight is given as 40.07. Further experiments will be necessary to obtain a more accurate value of the ratio and to examine the possibility of still fainter isotopes with other atomic weights. Accurate intensity measurements may be expected to involve considerable difficulty, since, if they are to indicate the relative proportions of the isotopes in the element, several conditions must be fulfilled; the faint background of scattered and reflected rays must be considered or suppressed, the intensity ratios must be independent of the particular experimental conditions used, the primary ionization must be unaffected by the alterations in the electric or magnetic fields used to bring a new component onto the slit, and the possibility must be considered that, as appears to hold in the case of lithium, the different components may have different rates of evaporation at different temperatures and with different surface conditions.

RATIOS OF COMPONENTS AND ATOMIC WEIGHTS.

It may be pointed out, however, that a reliable determination of the proportions of all the isotopes in an element by positive-ray measurements would allow conclusions to be drawn as to the existence or absence of a "packing effect" or a slight divergence of the atomic weight from an integral value. If the mean atomic weight calculated from the positive-ray ratios, on the assumption of integral values for the components, is lower than the chemical atomic weight, we must conclude that the components have atomic weights greater than exact integers by an amount sufficient to make up the difference. Thus the agreement of the mean atomic weight obtained for potassium with the chemical atomic weight, might be used as an argument that the atomic weight of the strong potassium component is exactly 39.00 to within one integer in the second decimal place. In the case of calcium we might use the low computed atomic weight 40.055 to deduce the value 40.07 − 0.055 = 40.015 as the correct atomic weight of the heavier component. More careful measurements of the intensity ratios will however be necessary before conclusions of this nature can have much weight.

Experiments with Zinc (Atomic Weight 65.38).

Strong rays were obtained from a zinc anode when heated to a very dull red temperature. Three strong and one faint maxima were observed, separated by two units on the atomic weight scale. It was found that the zinc lines were also obtained from a calcium anode to which a little zinc had been added. Probably due to the higher temperature the rays were then usually sharper than with pure zinc. The curve in Fig. 4 shows the different components observed with this anode. The first experiments with a zinc anode were made before those with calcium and

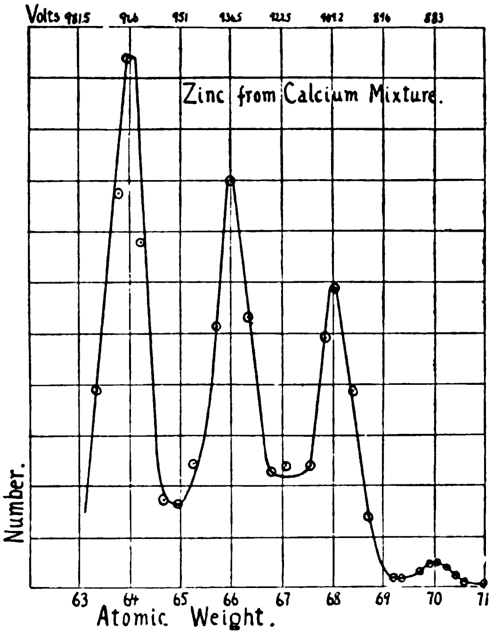

Fig. 4.

potassium, and before the two gauzes had been placed on each side of the slit in *P* (Fig. 1). These first experiments gave quite different intensity ratios for the components from that shown in Fig. 4, and a mean atomic weight almost a unit higher. An early curve is reproduced in Dr. Aston's book on Isotopes, p. 147. Later, with two different anodes containing mixtures of calcium and zinc, and with one containing very pure zinc, intensity ratios similar to that shown in Fig. 4 were obtained. The mean atomic weight from curve 4 is approximately 65.5.

It was suspected that the changes in the field between *P* and S_1, used to bring the different components on to the second slit, might have influenced the total intensity of the rays in the first experiments by means of the stray field through the slit in *P*. Two gauzes were therefore introduced as mentioned in the first paragraph. Intensity ratios similar to that shown in the curve were then always obtained from anodes of both pure and commercial zinc, and the total positive-ray current as indicated by a galvanometer was found independent of the field.

The accuracy with which the maxima of the three strong zinc components agreed with integral atomic weights is shown in Fig. 5. The center of each short line indicates the value taken as the maximum and the length of the line indicates the estimated error in the setting (usually ± 2 volts). It is seen that to the accuracy obtained the atomic weights are two integers apart.

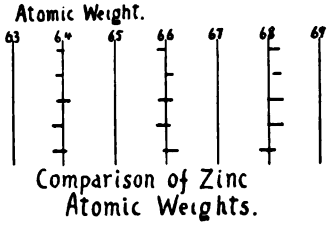

Fig. 5.

It was at first assumed that the atomic weights of the components were 63, 65, 67 and 69, since, with the intensities first observed, a mean atomic weight was obtained which agreed with the chemical atomic weight 65.38.[1] This reasoning was invalidated by the different intensity ratios obtained with the improved shielding, and a direct comparison with the calcium component at 40 showed the atomic weights to be near the integers 64, 66, 68, and 70. With a calcium anode to which a little zinc had been added rays of both elements were obtained, and the atomic weights could be compared by observing the potentials required to bring the different maxima on to the second slit, while the magnetic field was kept constant. The settings could usually be made with an uncertainty of 2 volts or less, and are illustrated in Fig. 6. The center of the short line represents, as before, the value taken for the maximum and the length of the line represents the estimated error. Thus the potentials in volts used in the first plot were 974 ± 2; 610 ± 1; 592.6 ± 1; 575.1 ± 2. The first three comparisons were made with one anode and the last three with a new filling and adjustment. It is seen that within the experimental error the atomic weights of the three zinc components are 64, 66, and 68. The faint isotope at 70 was not used in the comparisons with calcium since much more time and care is required in setting on it than on the stronger components.

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[1] Science, Vol. 54, p. 516, 1921.

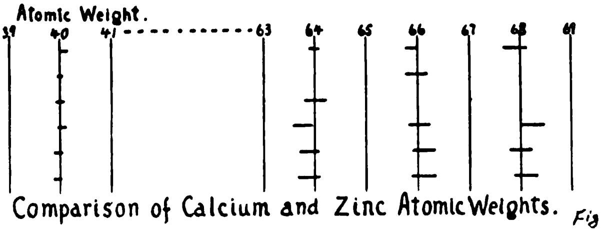

Fig. 6.

In all the curves drawn for the zinc rays the intensity at atomic weight 67 is greater than at 65, although the neighboring lines at 66 and 68 are weaker than 64 and 66. This is probably due to the existence of an unresolved isotope at 67, and in two curves a slight maximum was also indicated at this atomic weight. Experiments with sharper bundles will be necessary to decide definitely if a fifth isotope exists at 67 or not.

Resolving Power of the Apparatus.

The sharpness of the curves and the dependence on the slit width and other factors is of interest in connection with the possibility of improving the resolution sufficiently to analyze heavier elements. The slit widths used in all the experiments described in this paper were 0.37 mm. for the first, and 0.42 mm. for the second. If the focusing were perfect the width of the bundle at S_2 would be 0.37 mm. The curve in Fig. 2 is obtained as this bundle is moved from one edge of the slit S_2 across to the other, the displacement of the bundle in moving between the positions which give the currents A and B half way to the maximum being exactly the width of the bundle. From the relation M.V. = const. d^2, as discussed in the first paper,[1] we see that the beam must have had a width of 0.55 mm. in order to give the curve for potassium. The beam originally 0.37 mm. wide has thus increased in width by 0.18 mm. in going a distance of 17 cm. This extra width is probably due entirely to a lack of homogeneity in the velocity of the rays since a dispersion of only 3 volts in the 900 used would account for the extra width of the image. The sharpest curves observed with zinc indicate a width of 0.68 mm. at the second slit, and some experiments showed that the sharpness was affected to a considerable extent by the adjustment of the potentials between the plate *P*, the cathode and the anode.

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[1] A. J. Dempster, Phys. Rev., 11, p. 320, 1918.

If as great a uniformity in velocity can be obtained with heavier elements, as in the case of calcium or potassium, a considerable increase in resolution should be secured with narrower slits. Thus with $S_1 = 0.07$ mm. the beam should be 0.25 mm. wide at S_2 and the separation of the points *AB* on the atomic weight scale would be half a unit for an atomic weight of 100, so that all integral components less than this should be sharply separated. If the total potential were increased to 2,000 volts, elements as high as 200 in atomic weight should be similarly separated, provided the necessary magnetic field of 18,000 gauss could be secured.

Should it prove necessary to deal with a greater velocity dispersion than that found in the case of potassium and calcium, an electric field may be added to focus rays with slightly different velocities as in the apparatus designed by Dr. Aston. With slow rays it is also possible to combine the velocity focusing, for a single mass, with the direction focusing as used in these experiments. Figs. 7 and 8, in which *A* and *B* represent two rays diverging in direction, and *C* a ray of the same mass and smaller velocity, illustrate diagrammatically two arrangements of the magnetic and electric fields. In Fig. 7 the fields act simultaneously, and it may be readily shown that a small range of velocities is focused at S_2 when the electric force is half the magnetic and opposite in direction. In Fig. 8 the magnetic and electric fields, *M* and *E*, act separately, the velocity focusing occurring when the electric force is twice the magnetic.

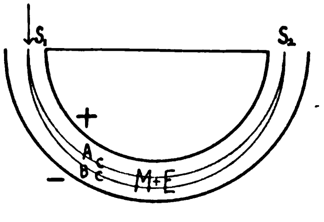

Fig. 7.

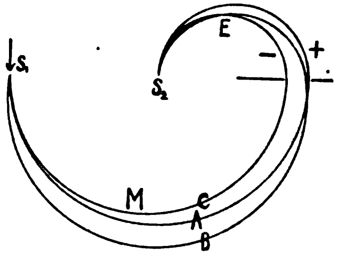

Fig. 8.

The author's thanks are due to Mr. F. B. Haynes for the use of the apparatus and method he developed for distilling calcium in vacuo, and to Mr. J. K. Morse for testing the calcium chemically for carbon dioxide.

RYERSON PHYSICAL LABORATORY,
July 21, 1922.

PROPERTIES OF ROCHELLE SALT RELATED TO THE PIEZO-ELECTRIC EFFECT.

By Joseph Valasek.

Synopsis.

Temperature variation of several physical properties of Rochelle salt, from – *30° to* + *30° C.*, was undertaken to determine which of them seem to be related to the piezo-electric effect, which increases rapidly between – 20 and – 15° C. and decreases rapidly between + 20 and + 30° C. In this way it was hoped to get information as to the nature of the structure underlying piezo-electric phenomena. *Refractive indices* were measured for the three principal directions for six wave-lengths from 4554 to 6500 Å. and at temperatures of – 70, – 11.5, 0, + 21.3 and + 40° C. The variation with temperature, however, is linear, the average coefficient being 59 × 10^{-6} per degree. The *thermal expansion* between – 10 and + 20° C. was measured by the Fizeau method for the three principal directions. The ratio of $(n^2 - 1)$ to ρ is approximately constant, in agreement with the Sellmeir formula for dispersion, and if the change in refractivity is regarded as due to the change in density, reasonable values are obtained for the constants in the Lorentz formula. The *specific rotatory power of an aqueous solution* of the salt was found to change less than 0.4° in the interval from + 4 to 40° C., giving no indication of a change in molecular asymmetry in this interval. The value obtained at 25° C. is 25.9° for sodium light, lying between the results of previous observers. The *electrical conductivity* increases only from 2 × 10^{-14} mhos/cm.^{3} at – 65° C. to 5.4 × 10^{-14} at – 20° C. Between – 20° and + 30° C., however, it was found to depend on the direction of the current, being only half as great in one direction as in the other at 0° and at 20°, and above 20° it increases very rapidly to 5 × 10^{-9} at 43°. At all temperatures, however, the current was found proportional to the applied field, at least up to 10,000 volts/cm. *The reversible electro-optic rotation* was observed in the direction of the field, using transparent alcohol electrodes and plane polarized light of wave-length 5737 Å. At 20° the rotation of the α and β axes in their plane per unit field normal to them is 1.7 × 10^{-4} degrees, and decreases for higher temperatures much as the dielectric constant does. The electro-optic constant e_{41} was also computed. Although Rochelle is classed as a type of crystal that should show no *pyro-electric effect*, a "real" effect was observed in the ă crystallographic direction as the crystal was gradually heated at a constant rate. The coefficient changes sign just below room temperature and becomes very large.

Theory of piezo-electricity is discussed briefly in the light of these results. In view of the fact that none of the properties measured show changes with temperature which correspond with those of the piezo-electric effect it is probable that the elastic or piezo-optic constants must change in such a way as to account for the piezo-electric changes.

Newman's Principle of Symmetry in Crystal Optics.—Rochelle salt, if it belongs to the hemihedral class of the orthorhombic system, seems to form an *exception* to this principle since most of its electrical properties in the direction of the ă axis depend on the direction of the field.

Infra-red absorption band for Rochelle salt is computed from the constants of the dispersion formula to be at about 55 μ.

THE experiments herein described were initiated for the purpose of examining some of the properties of Rochelle salt which might be related to the piezo-electric property and thus to obtain further information on the nature of the structure underlying piezo-electric phenomena. Rochelle salt is particularly suited for this study because its piezo-electric reaction is relatively large and because of the marked changes which occur in its activity at certain temperatures. As the crystal is heated from low temperatures, there is a sudden increase in activity between − 20 and − 15° C. and a corresponding decrease between + 20 and + 30° C. as the following table shows. The piezo-electric modulus given here is defined as the electric polarization in the a crystallographic direction per unit shear in the plane normal to it.

TABLE I.

Temperature.	Piez. Modulus.
− 70° C.	0.017 × 10^{-5}
− 50	0.017
− 30	0.065
− 20	1.08
− 10	6.07
0	6.75
+ 10	7.42
+ 20	8.10
+ 30	1.08
+ 40	0.41

In those temperature intervals where the piezo-electric property makes rapid changes, the writer has undertaken to study various other physical properties of the crystal. In the first place the variation with temperature was studied with the thought that the same type of structure may be responsible for both the piezo-electric property and the optical rotation or that they may be related in some way. Then again measurements were made on the indices of refraction because a shift in an absorption band caused by a changing restoring force of the ions producing the piezo-electric effect would be reflected in the indices of refraction if the absorption bands involved were not too far away from the visible region.[1] Furthermore, observations were made on the reversible electro-optic effect.

We shall begin by reviewing some general facts concerning Rochelle salt. This substance is a double tartrate of sodium and potassium with the chemical formula $NaKC_4H_4O_6 \cdot 4H_2O$. It crystallizes in the orthorhombic system, showing sphenoidal hemihedrism. It is optically active both as a crystal and in solution. It is, of course biaxial, as the crystal system shows. The structural formula is

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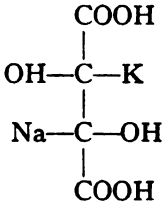
[1] Valasek, PHYS. REV., XIX., 478, 1922.



$$\begin{array}{c} \mathrm{COOH} \\ | \\ \mathrm{OH{-}C{-}K} \\ | \\ \mathrm{Na{-}C{-}OH} \\ | \\ \mathrm{COOH} \end{array}$$

This form has the usual type of asymmetry occurring in optically active carbon compounds. The crystal is brittle and soluble in water. This latter property enables one to cut it by a wet string running over pulleys and through water, and to polish it on a slightly moistened piece of ground glass. Since it cracks very easily due to unequal or too rapid temperature changes, it must be handled carefully. It cannot be heated above 53° C. as it transforms here into water and the single tartrates of sodium and potassium with an absorption of heat. A moderately sensitive differential thermocouple scheme indicates no sharp heat transformation anywhere between -70 and $+54$° C. On heating, however, there begins a slow and steady apparent heat evolution at 24° C. which continues up to 53° C. This is thought to be due to either an increase in thermal conductivity or to a steadily decreasing specific heat.

Refractivity.

The three principal indices of refraction were determined by a prism and spectrometer method for a number of wave-lengths. For measurement at various temperatures the crystal was mounted on a pedestal about ten centimeters high so as to be in the center of the double-walled vessel which contained the heating or cooling mixture. A cross-section of this arrangement is shown in Fig. 1*A*. Tubes *A* and *B* (1 x 2 cm.) served as passages for the light between the collimator and the telescope. Diaphragms *C* and *D* together with end plugs and plane-parallel windows served to cut down air circulation. The copper-constantan thermocouple which measured the temperature came up to the crystal through the hollow pedestal, which was largely made of thin-walled glass tubing. The cold junctions were kept in ice and the electromotive force was measured by a Leeds and Northrup Type K potentiometer. The thermocouple was calibrated at the fixed points given by fresh liquid air, frozen mercury, ice, and steam.

The prism used was cut from a large crystal about five centimeters along each edge, in such a way that one of the faces was a natural crystal face while the other was nearly parallel to the b and c crystallographic axes (Fig. 1*B*). In order to procure faces as flat as possible, a large prism was first cut and polished. From its center was cut the small prism about 2 cm.[3], which was used in the experiments. Diaphragms of black paper served to still farther cut down the areas of the faces, care being taken not to decrease the resolving power so much as to cause a noticeable lack of precision in setting on the spectrum lines. In this way a good double spectrum was obtained from which two indices could be determined. These indices will be denoted by n_1 and n_2 in the order of their magnitude.

The source of light was an arc between carbons containing barium chloride. This source gives a set of six bright lines fairly well distributed throughout the spectrum and proved to be very convenient for the determination of dispersion.

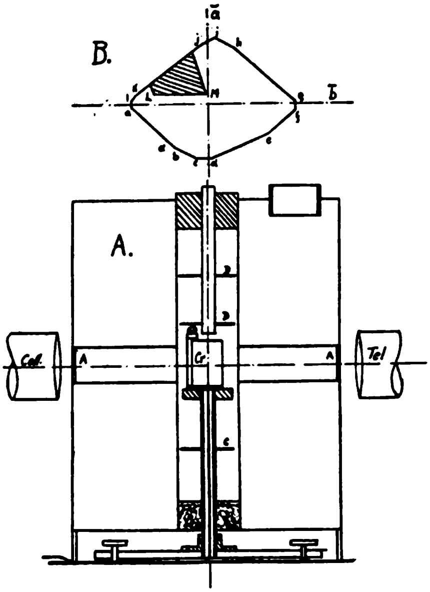


Fig. 1.
Mounting of prism for refractivity measurement.

In calculating the three main indices, Fresnel's formulæ for inactive crystals were used in spite of the fact that Rochelle salt is active.[1] This is permissible in this case because the indices were not measured closer than five units in the fifth decimal place and because the rotatory power of the crystal produced much smaller deviations from Fresnel's formulæ. Following Pockel's *Krystalloptik*, α, β, and γ will be used to denote the three main indices in the order of increasing magnitude and ν_1, ν_2, and ν_3 to denote the direction cosines of the wave normal in the crystal with respect to the principal axes. The indices n_1 and n_2 in an equatorial plane $\nu_1 = 0$, that is, normal to the α axis of the index-ellipsoid, will be given by the two n roots of the equation:

$$\left\{\frac{1}{\alpha^2} - \frac{1}{n^2}\right\}\left\{\left(\frac{1}{\gamma^2} - \frac{1}{n^2}\right)\nu_2^2 + \left(\frac{1}{\beta^2} - \frac{1}{n^2}\right)\nu_3^2\right\} = 0. \qquad (1)$$

In this plane, one of the indices, namely $n_1 = \alpha$, should be the same in all directions. This was found to be accurately true and is taken to justify our use of the simpler formula.

The orientation of the crystal was roughly as shown in Fig. 1 *B*, the

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[1] Pockels, Krystalloptik, 31.

LM face being normal to the ă axis within three degrees as determined from the crystal angles. The middle and greatest indices were calculated from formula (1) by solving for β and γ when measurements of n_2 had been made for two known directions. The value of β so found differed by only 0.00002 from the value of n_2 normal to the face LM. The two directions chosen were normal to the faces of the prism.

The crystal was clamped in place by the edge facing the collimator so that when its angle changed due to anisotropic expansion[1] the light would still be normally incident on this face. If the constants for the two directions are respectively unprimed and primed, the following set of formulæ give the indices:

$$
\begin{aligned}
n_1 &= \frac{\sin A_1}{\sin (A_1 + D_1)}, \quad \text{etc.,} \\
\alpha &= n_1 = n_1', \\
\beta^2 &= \left(\frac{\nu_3}{\nu_2\nu_3' - \nu_3\nu_2'}\right) n_2' - \left(\frac{\nu_3'}{\nu_2\nu_3' - \nu_3\nu_2'}\right) n_2, \qquad (2) \\
\gamma^2 &= \left(\frac{\nu_2}{\nu_2\nu_3' - \nu_3\nu_2'}\right) n_2' - \left(\frac{\nu_2'}{\nu_2\nu_3' - \nu_3\nu_2'}\right) n_2.
\end{aligned}
$$

The angles of the prism A and the angles of deviation D were measured on the spectrometer by standard methods at a number of steady temperatures between − 70 and + 40° C. A nicol prism was used in front of the eyepiece to keep the two spectra distinct.

A set of careful determinations of the three indices was made in this way for the six lines of the barium spectrum at room temperature with the windows of the cooling chamber removed. These are given in Table II.

TABLE II.

Temperature 21.3° C.

Wave-length.	α.	β.	γ.
4554.2 Å.	1.49906	1.50062	1.50504
4934.2	1.49565	1.49734	1.50154
5535.7	1.49170	1.49348	1.49721
5853.9	1.49001	1.49183	1.49540
6141.9	1.48878	1.49056	1.49430
6497.1	1.48743	1.48920	1.49280

The directions of the α, β, and γ axes of the index ellipsoid are respectively the same as the directions of the c, b̄, and ă crystallographic axes.

Above and below room temperature, coverglasses cemented on with

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[1] Voigt, Krystallphysik, 276.

Canada balsam had to be applied to preserve the polish of the prism. With the apparatus entirely assembled another set of determinations was made at the same temperature and corrections found for the cover-glasses and windows. The indices were then measured for steady temperatures of − 70, − 11.5, 0.0, + 21.3, and + 40° C. The angle of the prism at these temperatures was measured by a reflecting eyepiece.

The main indices were calculated and plotted and it was observed that their variation with temperature was practically linear. From the best set of straight lines through the points the following values were obtained for the indices at 0° C. and for the temperature coefficients.

TABLE III.

Wave-length.	Indices at 0° C.	Temp. Coefficient.
	1.5004	0.000064
4554.2	1.5019	58
	1.5063	68
	1.4970	63
4934.2	1.4987	58
	1.5029	65
	1.4930	64
5535.7	1.4947	58
	1.4986	63
	1.4913	61
5853.9	1.4930	60
	1.4968	58
	1.4900	61
6141.9	1.4917	58
	1.4953	61
	1.4888	63
6497.1	1.4905	59
	1.4939	59

The values of α and β in both tables are more accurate than those of γ because the latter are obtained by solving the equation of the oval for its major axis which is respectively about 90° and 40° from the directions of the radii measured. In Table II. the values of α and β are good to $\pm$ 0.00005, while γ is good to $\pm$ 0.00015. The values in Table III. may be in error by greater amounts because of the greater variety of chances for error that present themselves in measurements at other than room temperature.

A surprising outcome of these measurements is that there is no marked change in optical properties between − 70 and + 40° C. This was contrary to expectation and shows that there is no gross change in crystal structure occurring between these temperatures. This eliminates one explanation that may be advanced for the variation in piezo-electric response that occurs in this range.

Drude's dispersion theory applied to this data gives a little information as to the nature of the bound charges. The best set of observations for this purpose is the α set given in Table II. since it is checked by a greater number of independent observations and is a directly measured result. Suppose we take the five-constant formula:[1]

$$n^2 = -B'\lambda^4 - A'\lambda^2 + A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}. \tag{3}$$

According to the theory the constants should all be positive and respectively given by the formulæ:

$$\begin{aligned} B' &= \sum \frac{\theta_r}{\lambda_r^2}; \qquad A' = \sum \frac{\theta_r}{\lambda_r^4}; \\ A &= 1 + \sum \theta_v; \qquad B = \sum \theta_v \lambda_v^2; \qquad C = \sum \theta_v \lambda_v^4, \end{aligned} \tag{4}$$

where the subscript r means that the summation is to be carried out only for charges whose free period lies in the infra-red, while v refers in a similar fashion to the ultraviolet charges, and θ is the contribution of each type to the dielectric constant. If there is only one predominating type of each, the summation signs can be removed and we have

$$\lambda_r^2 = \frac{K - A}{A'}, \tag{5}$$

where K is the ordinary dielectric constant and

$$K = 1 + \sum \theta_v + \sum \theta_r = A + \sum \theta_r. \tag{6}$$

Evaluating the constants of (3), it is found that

$$\begin{aligned} B' &= -\ 0.163, \\ A' &= +\ 0.215, \\ A &= +\ 2.282, \\ B &= -\ 0.007, \\ C &= +\ 0.002. \end{aligned}$$

Since K has the value 645 at 20° C., it is found that the infra-red absorption band should be at 55 microns.

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[1] Drude, Optik,

Inspection of the values above shows that the constants B and B' have the opposite sign to that which the theory gives. The observations are considered to be fairly reliable as measurements on several crystals show, so that the sign is not due to error.

In a previous paper the writer has calculated the position of an absorption band from piezo-electric data.[1] The expression used was derived on the assumption that $\alpha = 1/3$, where this α is defined by the relation $E = E_p + \alpha P$, and E_p is the field at a charge in a medium whose polarization is P. It will be shown in the following that α is far from 1/3 for Rochelle salt, but that this constant can be eliminated anyway. The equation for the X component of vibration of an ion of charge e and mass m is:

$$m\ddot{\xi} = eX - 4\pi e^2\left(\frac{1}{\theta} - \alpha N\right)\xi. \tag{7}$$

The wave-length of the free vibration is then

$$\lambda = \left\{\frac{c^2\pi m}{e^2}\left(\frac{\theta}{1 - \alpha N\theta}\right)\right\}^{1/2}. \tag{8}$$

If the contribution of this ion to the dielectric constant is K_r and there are N such ions per cubic centimeter, then

$$K_r = 1 + \frac{N\theta}{1 - \alpha N\theta} \tag{9}$$

and we have

$$\lambda = \left\{\frac{c^2\pi m(K_r - 1)}{Ne^2}\right\}^{1/2}, \tag{10}$$

which is independent of α but contains K_r. Since this is very nearly equal to the entire dielectric constant between − 20 and + 20° C., we shall replace K_r by K. The difference between these two quantities is the constant A of the dispersion formula and K is well in the hundreds at these temperatures. The quantities N, m, and e are unknown, but it should be interesting to try some possible values. For convenience let us rewrite the expression by putting S equal to the sum of the atomic weights of the atoms in this ion, letting σ be the sum of the chemical valencies, and u be the number of such ions in each molecule. Then we have:

$$\lambda_r = 0.741\sqrt{\frac{(K - 1)S}{\sigma^2 u}}. \tag{11}$$

Since the infra-red ions are always of atomic or molecular magnitudes and because the water of crystallization is so important to the piezo-electric properties, it may be that either the O or the OH ion is the important one. Taking the value of K as 645 at 20° C., it is found that the natural wave-length for the two cases above is respectively 9.5 and 40. The latter gives the better agreement with the value found from the dispersion theory. It must be admitted that there are many arbitrary assumptions in the above. This, however, is as much as can be done at present.

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[1] PHYS. REV., XIX., 489.

The temperature coefficients of the indices given in Table III. turned out to be relatively large. This would ordinarily mean that the coefficient of volume expansion is large. On either Drude's or Lorentz's dispersion theory, the variation in the indices of refraction of any single chemical compound should be dependent entirely on the variations in the numbers of dispersion charges per unit volume. This number varies inversely as the density. The Lorentzian relation[1] between index of refraction n and density ρ may be written in the following form:

$$\frac{1}{\rho} = \frac{C}{n^2 - 1} + C\alpha, \tag{12}$$

where

$$C = \frac{1}{\rho} \sum \frac{\nu_s^2 e_s^2}{m_s(p_s^2 - p^2)}. \tag{13}$$

Knowing n and ρ at various temperatures enables one to find the constants C and α and to test the theory.

THERMAL EXPANSION.

To find the variation in specific volume with temperature, the coefficients of linear expansion were measured in the three principal directions by the Fizeau method.[2] A plan of the apparatus is shown in Fig. 2. The three tripods which supported the optical surfaces were made of iron so as to expand very much less than the crystal. A thermocouple T.C., whose junction nearly touched the crystal, was used to measure the temperature. The movement of the rings between two steady temperatures was observed in the telescope Tel. The apparatus had to be sealed to exclude moisture; otherwise this would condense on the small tripod points p and cause them to sink in. The way this occurred is interesting. The inset in Fig. 2 shows a cross-section of one of the pits.

In each of the crystallographic directions a set of measurements of the relative expansion of crystal and apparatus was made for the temperature interval of − 10 and + 20° C. using a cube of Rochelle salt. The dimensions of the cube were: 1.302 × 1.271 × 1.163 cm. and its faces were cut and polished within 3° of normal to the crystallographic axes. The expansion of the apparatus was measured by using a cube of lead whose coefficient was taken to be 0.00002726. This cube was cut from a Bureau of Standards melting point sample and was nearly pure. The average coefficients of expansion between − 10 and + 20° C. for Rochelle salt were thus found to have the values:

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[1] Richardson, Electron Theory, p. 148.

[2] Tutton, Crystallography, p. 884.

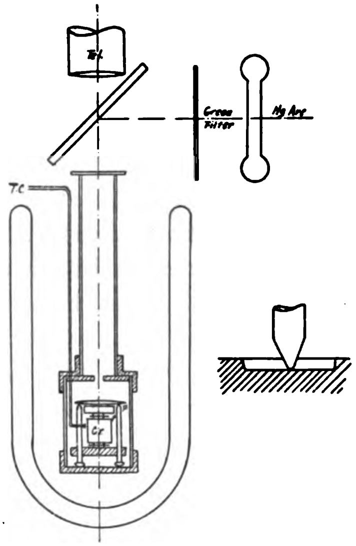

Fig. 2.
Dilatometer.

$$a = 0.0000599 \pm 4,$$
$$b = 0.0000381,$$
$$c = 0.0000448.$$

The coefficient of volume expansion is accordingly:

$$\Delta = 0.0001428.$$

Since the density of Rochelle salt at 0° C. was found to be 1.766 we have for any other temperature; θ°C:

$$\delta = 1.766 - 0.0002522\,\theta.$$

As noted above these values are the averages over a temperature range of thirty degrees extending from − 10 to + 20° C. Lower temperatures could not be conveniently kept steady for a long enough period of time, while at higher temperatures there was trouble due to condensation of traces of moisture on the crystal as soon as the surroundings were warmed. Unless the end temperatures were steady for about half an hour one could not obtain very reliable results as it took that long to be sure that the fringes were perfectly steady. It was desirable, however, to see if a change in dimensions could be detected at − 20° C. where the crystal became active. Observation of the movement of the fringes during a slow and uniform rate of heating of 2° per minute from the temperature of carbon-dioxide snow gave a smooth curve for all three crystallographic directions. There can be no abnormal change in dimensions comparable with the wave-length of mercury-green light unless this is spread out over a range of about ten degrees or more.

According to the Lorentz formula (12) there is a linear relation between

$1/\rho$ and $1/(n^2 - 1)$. This gives a set of three straight lines for any one wave-length, whose slopes are C_1, C_2, and C_3, and whose y intercepts are $C_1\alpha_1$, $C_2\alpha_2$, $C_3\alpha_3$. The values of α are of interest as bearing on the effect of surrounding polarization on the dispersion charges. For a cubical arrangement of charges it is found to be equal to one third. Drude, in his dispersion theory, assumes that the force on the dispersion charges is equal to the electric vector of the incident wave times the charge, that is, he puts α equal to zero. This theory leads to the Sellmeier type of formula. Lorentz's formula differs from this only in so far as no assumptions have been made regarding the value of α.

The values of C and α given by the best straight lines through the calculated points are as follows:

Table IV.

Wave-length.	C.	$\frac{n^2-1}{\rho}$.	α.
4554.2	0.706 0.729 0.660	0.716 0.710 0.707	0.003 0.080 0.068
5535.7	0.660 0.718 0.657	0.705 0.698 0.695	0.043 0.078 0.043
6497.1	0.648 0.673 0.683	0.696 0.690 0.689	0.041 0.021 0.017

The values of α are evidently much nearer zero than one third and the dispersion should be fitted fairly well by Sellmeier's formula. The values of C roughly agree with $(n^2 - 1)/\rho$ as the table shows. This agreement should be perfect when α is zero.

The values of C and α above are calculated so that the variation of the index of refraction with temperature is accurately accounted for by the dilatation of the crystal. Since their values are not unreasonable, at least the bulk of the change in indices can be so accounted for.

The variation in C must be all due to changes in the natural period p_e for any one color. The above values show that the absorption bands for the three principal indices are substantially the same in the infra-red but may differ in the ultraviolet. The small α means that the force on a unit charge per unit polarization is small, just as though the charge were well shielded.

Optical Activity.

Since the optical activity and piezo-electric property always occur simultaneously in crystals having an asymmetric structure, it was decided to study the optical activity of Rochelle salt. Substances forming such crystals may be rotatory when dissolved or melted, like Rochelle salt and sugar, or they may be only active in the crystalline state, like quartz. If they are active in the non-crystalline condition, it is due to an asymmetric molecular structure. Such substances are as a rule carbon compounds and the asymmetry may be pictured by a structural formula in space in which the four radicals combined with the carbon atom are placed at the corners of a tetrahedron. J. J. Thomson[1] has shown that in the case of active solutions the molecules must have both dynamic and electric asymmetry, while in a crystal either type is sufficient to produce activity.

There is reason to believe that the piezo-electric property is rather due to inter-molecular reactions in the crystal structure, so that naturally, it would be best to measure the rotatory power of the crystal in the directions of the optic axes. This has been done at ordinary temperatures by Pocklington[2] and is the first such determination for a biaxial crystal. He found that the plane of polarization of sodium light was rotated − 1.2° per millimeter in the directions of both binormals. This work was repeated and extended to other crystals by Dufet, who found for Rochelle salt − 1.35 instead of − 1.2. There is difficulty in carrying out such measurements at different temperatures because of the movement of the optic axes.

The rotatory power of the solution can, however, be measured without much difficulty, but the range of temperatures is very limited and covers only that one of the critical points which is at room temperature. At any rate some alteration in molecular structure may be detected here. One may suppose, moreover, that a change in molecular structure would be the basis of any change in crystal structure.

Observations were accordingly made on the rotation by a solution of a crystal of Rochelle salt in water. A ten-centimeter polarimeter tube was inserted in a double-walled chamber which could be filled with water and heated electrically. The temperature was measured by a copper-constantan thermocouple whose junction was tied to the center of the polarimeter tube. The brass ends of the tube were coated by a thin film of paraffin to keep the solution from attacking them and becoming contaminated.

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[1] J. J. Thomson, Phil. Mag., Dec., 1920.

[2] Pocklington, Phil. Mag. (6), II., 368, 1901.

The concentration of the solution was determined by evaporating a carefully weighed portion in a hot water bath and then drying the residue under a bell-jar with P_2O_5 in vacuo until the weight showed no further diminution. The remainder was assumed to be the anhydrous salt. The concentration used was 0.264 grams of the anhydrous salt per cubic centimeter of solution at 4° C. The density of the solution decreases by about a half per cent. between 4 and 30° C. Effects of expansion of the polarimeter tube are negligible.

The specific rotations for sodium light are shown plotted against temperature in Fig. 3.

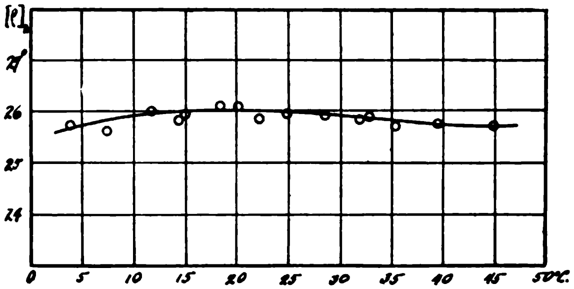

Fig. 3.

There seems to be a considerable lack of agreement between values given by various investigators for the rotatory power of Rochelle salt solution and the present value does not agree with any of them. In Dufet's tables the following figures are given:

$[\rho]_D$	Concentration.	Authority.
22.42.......	c = 20 hydr.	Krecke, 1872.
29.67.......	c = 10.77 anh.	Landolt.
29.5........	c = 21.0 anh.	Kummel, 1891.
29.53.......	c = 9 to 43 anh.	Thomsen, 1886.
22.12.......	c = 5 to 45 anh.	Long, 1888.

The concentration is given in grams per one hundred cubic centimeters of solution. The present value comes just between the two extremes.

The differences can hardly be due to error in measuring the rotation so that it seems that they must be due to differences in taking care of the water of crystallization in calculating the concentration, or possibly due to a very impure salt. The writer has also checked his result by measuring the rotation by a weighed amount of hydrated Rochelle salt in a weighed amount of water. The weight of the water of crystallization was calculated from molecular weights and subtracted from that of the salt and added to that of the water. Using the density of water the grams of anhydrous salt in a cubic centimeter of solution was found. The final results were 26.4 and 25.8 on two different trials.

In conclusion, however uncertain the value of $[\rho]$ is, it is at least evident that no marked change in rotatory power occurs at 20° C. The molecular structure which accounts for optical rotation is therefore independent of the piezo-electric structure.

ELECTRICAL CONDUCTIVITY.

In a recent paper the writer has reported a variation in electrical conductivity of Rochelle salt with temperature.[1] It appeared that there was a very marked and continuous increase in conductivity beginning at 23° C. when the crystal was heated at a uniform rate from the temperature of carbon-dioxide snow. Under normal conditions the crystal was about as good an insulator as ordinary glass when the surfaces were dry and the temperature was less than 23° C. There has been recently reported[2] an increase in conductivity for alternating currents even at temperatures below 23° C. when the field exceeds about 3,500 volts per centimeter. In view of this it seemed advisable to extend the writer's work on conductivity for direct currents by making measurements for various applied fields at different temperatures.

The conductivity was determined by measuring the current through the crystal by a sensitive galvanometer and the voltage across it by an electrostatic voltmeter. The galvanometer was of 650 ohms resistance and was shunted by 20,000 ohms so as to be nearly aperiodic. Its sensitivity under this condition was 1.108×10^{-9} amperes per millimeter deflection.

The direct electromotive force was furnished by a transformer giving up to 10,000 volts in connection with a rectifier. A Coolidge tube proved convenient for rectification since the current was only enough to take care of insulation leakage. The diagram of connections is shown in the figure below. The battery of Leyden jars across the terminals was of sufficient capacity to keep the system charged for several seconds after the transformer was cut off.

The leads were soldered to the tinfoil plates which were cemented to the crystal with shellac. To one of the plates there was also soldered a copper-constantan thermocouple to measure the temperature of the crystal. To help reduce errors due to surface leakage, the tinfoil plates did not extend closer than two millimeters from the edges of the plate.

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[1] PHYS. REV., XIX., p. 488.

[2] J. G. Frayne, Wash. Meet. of Am. Phys. Soc., April, 1922.

The surfaces were dried by phosphorus pentoxide and then coated with paraffin. The sample so prepared was suspended by the leads in the center of a large glass test tube. The wires were sealed through glass tubes which passed through the stopper. Diaphragms, wool plugs, and a brass cylinder helped to keep the temperature uniform. The tube containing the crystal was cooled by cold packs or baths or heated by the electric heater which surrounded it.

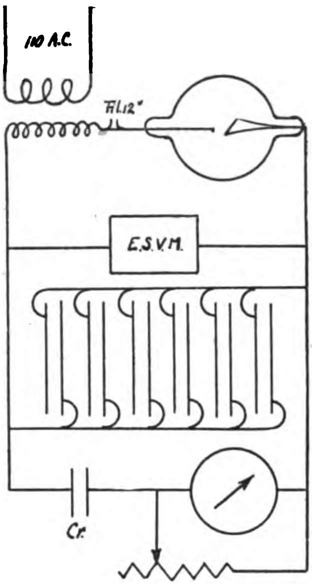

Fig. 4.

It was soon realized that when the applied potential became too great there was a corona discharge off the edges of the tinfoil. The first noticeable increase in conductivity due to this cause came at about 12,000 volts per centimeter through the crystal. There is reason to believe that the apparent increase in conductivity for alternating fields in the work referred to above is due to corona unless special precautions were taken to eliminate it. Experiments show that the corona loss may start at much lower potentials if the electrode edges are not separated or protected in some way.

For Rochelle salt it was found that no marked increase in conductivity or other deviation from Ohm's law occurs below 10,000 volts per centimeter and probably none below double that field.

The conductivity was found to depend on the direction of the current for some temperatures. This occurred in the range of maximum piezoelectric activity, the greater conductivity being in the direction, (+), of the permanent polarization.[1] Even in this case the relation of current to field was linear within the above field limits.

TABLE IV.

Temperature.	Conductivity.
$-65°$ C.	2.0×10^{-14} mhos/cm.^{3}
-40	3.6×10^{-14}
-20	5.4×10^{-14}
0	$+9.0 \times 10^{-14}$ and -5.0×10^{-14}
$+20$	$+22.0 \times 10^{-14}$ and -11.0×10^{-14}
$+30$	$+11.8 \times 10^{-13}$ and -11.1×10^{-13}
$+35$	1.00×10^{-11}
$+43$	5.00×10^{-9}

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[1] Phys. Rev., XVII., p. 476.

Values at higher temperatures will be found in one of the writer's papers.[1]

In the paper just referred to, it was reported that the crystal begins to conduct at 23° C. What was really meant was that conduction below this temperature seemed negligible. This, of course, depends on the sensitivity of the instruments used and on the scale in plotting curves. By changing these, apparently sharp bends in exponentially increasing curves may be put nearly anywhere. As the above table shows, there are no sharp breaks in the conductivity curve.

It is interesting that the conductivity is different for currents in opposite directions in the temperature range where the crystal is piezo-electrically active. The significance of this is not fully understood but it seems to be connected with the permanent polarization and related polar effects as will be pointed out in the concluding discussion. If the polarization were not so small, this would be in accordance with Thomson's theory of conduction, the essential feature of which is the shooting of electrons from atom to atom by a sort of radio-activity induced by the field.

ELECTRO-OPTIC EFFECT.

The reversible electro-optic effect in acentric crystals has been studied for several substances, including Rochelle salt, by F. Pockels.[2] These types of crystal are always piezo-electric and exhibit an electro-optic effect analogous to the Kerr effect except that the polarization constants vary in a linear manner with the field instead of the square. Pockels' observations have considerable theoretical interest because he was able to show that the effect is only partly due to the mechanical action of the electric field and that there is a part due to a direct influence of the applied field on the vibrations of the charges in the medium. This change in the periods, which is analogous to the Stark effect, affects the optical properties of the substance.

To completely determine any general variation in the optical properties of a crystal, the positions and magnitudes of the three main indices must be fixed. This may be done by six quantities called polarization constants or optical parameters.[3] Pockels develops a set of formulæ by first writing the most general expression for each of these parameters in the form of a power series in ascending powers of either the field or the polarization. The reversible electro-optic effect must be expressible in odd powers alone, and for fields not too great, this may be taken as the first. This effect is observed in all acentric crystals and in no other types. The irreversible or Kerr effect must be an even function of the field and as a first approximation, the first may be taken. This effect is observed in all substances but needs a relatively greater field to bring it into prominence. These general formulæ are then simplified by considering the symmetry of the particular crystal system to which they are to be applied. This is done by adjusting the coefficients so as to put the equations into such a form that transformations of the axes into physically equivalent positions keeps their form invariant. These physically identical positions are found by a consideration of crystal symmetry which is their most general manifestation. The equations for the hemihedral class of the orthorhombic system are:

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[1] PHYS. REV., XIX., p. 488.

[2] Pockels, Krystalloptik, p. 492, and Voigt, Magneto- u. Elektro-optik, p. 341.

[3] Pockels, Krystalloptik, p. 66.

$$\begin{array}{lll} a_{11} = a_0^2; & a_{22} = b_0^2; & a_{33} = c_0^2. \\ a_{23} = e_{41}P_x; & a_{31} = e_{52}P_y; & a_{12} = e_{63}P_z. \end{array} \tag{15}$$

In these equations a_{11}, etc., are the six polarization constants; a_0, b_0, c_0 are the initial values of the principal wave-velocities; P_x, P_y, and P_z are the components of the polarization, which is assumed to be a linear function of the field, and e_{41}, e_{52}, and e_{63} are the three remaining constants which describe the electro-optic behavior of this class. These formulæ show that since the first three parameters do not change, the only effect in this type of crystal is the rotation of the principal axes around the lines of force. If the components of the rotation are ϕ_x, ϕ_y and ϕ_z then

$$\tan 2\phi_x = \frac{2a_{23}}{a_{22} - a_{23}}, \qquad \text{etc.,}$$

or (16)

$$\tan 2\phi_x = \frac{2e_{41}P_x}{b_0^2 - c_0^2} = \frac{K_x - 1}{2\pi(b_0^2 - c_0^2)} \cdot e_{41}X.$$

Values given by Pockels to the constants of Rochelle salt are:

$$e_{52} = -10.8 \times 10^{-8}; \qquad e_{63} = +2.1 \times 10^{-8}.$$

He remarks that the value of e_{41} could not be definitely determined because of the strong internal conductivity in this direction, but still that it was found to be negative and of the same order of magnitude as e_{52} or perhaps greater. In some cases of other crystals he was able to calculate how much of the effect was due to electric deformation, but in the case of Rochelle salt the necessary data on elastic constants and piezo-optic coefficients was lacking. The sign of e_{63}, however, is opposite to what it would be if all the effect were due to electric deformation so that there is surely a direct electro-optic effect in this case at least.

In the ă direction Pockels found also an increase in double refraction, *i.e.*, a Kerr effect, and states that this might be related to the large internal conductivity in this direction. The conductivity of the crystal is, however, not particularly large under ordinary conditions as the preceding pages show.

The present work is concerned with the variation in the electro-optic effect near the upper, more accessible, critical piezo-electric temperature range. Whereas Pockels calculated the rotation of the principal axes by observing the change in double refraction in some known direction in the plane normal to the field, the writer sought to measure the effect more directly. The most convenient arrangement was considered to be one in which transparent electrodes were applied to the faces of the crystal so that observations could be made in the direction of the lines of force. For this purpose, alcohol electrodes were used since this substance does not dissolve the crystal while its conductivity is 10^5 times as great as that of Rochelle salt at the temperatures employed. The arrangement used in mounting the crystal plate is shown in Fig. 5. A difference of potential was applied between the platinum rings *BB* which were near the crystal and in the tubes containing the alcohol. The crystal was clamped between the rubber tubes *CC* by the screws *DD* running through the hard rubber blocks *EE*. The plane-parallel windows *AA* were cemented on with paraffin. A thermocouple T.C. came under one of the rubber tubes close to the crystal. To minimize electrical leakage over the surfaces the plate was made as large as possible so as to present a maximum distance around the edges. The alcohol had to be free of water so as not to spoil the faces of the plate. The difference of potential was applied and measured by the same scheme as used in the conductivity measurements.

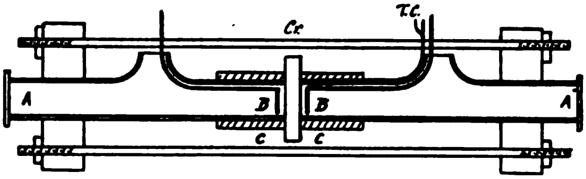

Fig. 5.

The monochromatic light used in the measurements was furnished by a Hilger wave-length spectrometer in connection with an arc light. For most purposes the brightest illumination obtainable gave the best results. This proved to be the yellow-green of 5737 Å. A lens and nicol prism were placed in the beam so that plane polarized parallel light could be transmitted through the crystal plate in the direction of the applied field. The resulting elliptically polarized light was analyzed by A. Q. Tool's modification[1] of Stokes's analyzer which was kindly loaned to the writer by the University of Nebraska.

For any crystal plate with relative retardation δ and orientation ϕ with respect to the plane of polarization of the incident light, the angle ω whose tangent is the ellipticity is given by the equation:

$$\sin 2\omega = \sin 2\phi \sin \delta. \tag{17}$$

For a Stokes's analyzer of compensator order πN_1 which is set on this ellipse we have:[2]

$$\sin 2\omega = \sin 2\pi N_1 \cos n,$$

where

$$\cos 2\pi N_1 = \frac{\tan n}{\tan c} \tag{18}$$

and n and c are respectively the differences between complementary compensator and nicol settings. Combining these two equations and differentiating, we find that:

$$-\sin 2\pi N_1 \cdot \sin n \cdot \Delta n = 2 \cos 2\phi \cdot \sin \delta \cdot \Delta\phi + \sin 2\phi \cdot \cos \delta \cdot \Delta\delta. \tag{19}$$

Suppose that the plate is set so that $\phi = 0$. Then if the compensator is very nearly a quarter wave plate and the ellipticity is small so that n is nearly $\pi/2$, we have as more or less of an approximation according to the accuracy with which these conditions are fulfilled:

$$\Delta n = 2 \sin \delta \cdot \Delta\phi. \tag{20}$$

The relative retardation δ can be calculated from the indices and the thickness of the plate. For the best accuracy the thickness should be such that $\sin \delta$ is nearly unity. The value of δ is given by:

$$\delta = \frac{2\pi d}{\lambda}(n_1 - n_2). \tag{21}$$

For light of wave-length 0.00005737 cm., δ is equal to 19.75 d, so that d should best be 2.00, 2.15, 2.31, 2.47, etc., millimeters and not 2.39, 2.55, etc. At the proper thickness a change in δ has a negligible effect on Δn, as equation (19) shows. By choosing such a thickness, errors due to temperature and ordinary electro-striction are eliminated.

A suggestion for improvement in apparatus and method is to mount the crystal on a graduated circle, and, having set the analyzer for plane polarized light, find the rotation of the crystal necessary to restore it. This would measure the angle $\Delta\phi$ directly. The writer did not have a circle available to carry this out.

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[1] Tool, Phys. Rev., XXXI., p. 1, 1910.

[2] Tuckerman, Univ. of Nebr. Studies, IX., No. 2, 1909.

The results of the observations are presented in Fig. 6, curve *A*. The ordinates give the rotation in degrees of the α and β axes in their plane per volt per centimeter normal to them. The fields used were about 8,000 volts per centimeter. The rotation reverses with the direction of the field and bears a right-hand screw relation to the directions of the lines of force. Referring to equation (16) the constant e_{41} was found to have the values:

$$- 1.94 \times 10^{-8} \text{ at } 20^\circ \text{ C.},$$
$$- 2.66 \times 10^{-8} \text{ at } 25^\circ \text{ C.},$$
$$- 2.76 \times 10^{-8} \text{ at } 30^\circ \text{ C.}$$

In computing these, the fields were put in electro-static units and the values of the dielectric constant used were those determined by the writer and are plotted in Fig. 6, curve *C*.

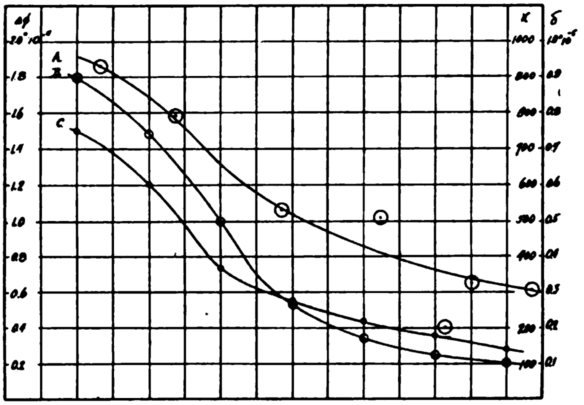

Fig. 6.

There is a decided decrease in the angular rotation as the temperature changes from 20 to 30° C. and the field is kept constant. To show the variation in piezo-electric modulus and dielectric constant in the same range, curves *B* and *C* are drawn. A comparison with curve *A* shows that the decrease in electric-optic rotation is less than that of either the piezo-electric modulus or the dielectric constant, although it is more nearly equivalent to the latter. Indeed, one observes that e_{41}, which refers to the rotation per unit polarization, increases continuously throughout this range.

This is a very striking result in view of the fact that the piezo-electric modulus decreases so appreciably. If the elastic coefficients and the piezo-optic constants do not change then the portion of the electro-optic effect due to electric deformation decreases in the same manner as the piezo-electric moduli. The direct effect of the field on the vibrations of the dispersion charges would then necessarily increase and soon give nearly the whole effect. As this is improbable, it seems that there is a decided change in the elasticity or the piezo-optic coefficients or both. In the absence of definite data on these quantities no more can be said at present. The writer inclines to the view that an increase in elastic constants occurs sufficient to account for both the variation in the piezo-electric moduli and the increase in the electro-optic effect.

Pyro-electric Effect.

Although Rochelle salt is classed as a type of crystal that should give no pyro-electric effect, still the existence of a measurable polarization in the $\breve{a}$ direction makes it possible that such an effect can be observed. The greatest difficulty in measuring it is the danger of exciting a piezo-electric effect due to non-uniform heating. Customarily, the charges which appear on the faces of the crystal are measured between two steady temperatures so that these errors tend to cancel out. Due to the difficulty of producing liquid insulating baths of steady temperature in the range to be investigated and because of the likelihood of leakage, a slow rate of heating was employed. The utmost precautions were taken to keep the heating uniform. The crystal plate was made circular so that the residual thermo-elastic stresses would have a symmetrical distribution and balance their piezo-electric action. This plate was suspended by the leads inside two concentric cylinders of brass. Copper diaphragms and plugs of wool in the ends served to make the temperature distribution uniform. To test the symmetry of the heating, measurements were made with the crystal in two positions at 90° to each other so as to give the complementary distribution of stresses. This just reversed the error due to the piezo-electric effect.

The charge was measured as it appeared on the faces, beginning at − 70° C., by an electrometer compensating system. This always kept the faces of the crystal nearly at zero potential and eliminated leakage to a large extent. In Fig. 7 several curves are shown which give as ordinates, the pyro-electric charge developed between − 70° C. and the temperature plotted as abscissa. Curve *C* gives the results obtained with the crystal rotated 90° to its previous position.

Attention is rather called to the general nature of these curves than to numerical values although it may be noted that the electrode area was 1.44 cm.^{2} The piezo-electric error has been largely eliminated for it will be observed that the results were very similar in the complementary positions mentioned above. In addition to this, the variation with temperature does not approach the magnitude of that shown by the piezo-electric charge for constant stress. The heating rate was constant and this should have made the stresses nearly constant. These facts all point to the pyro-electric character of the charge measured.

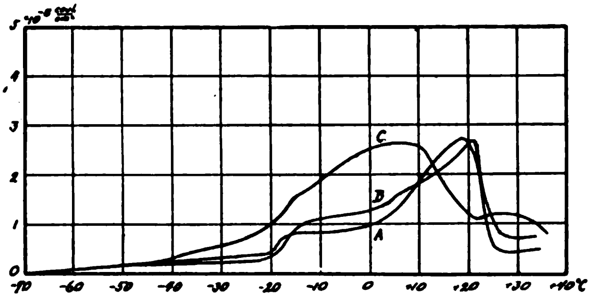

Fig. 7.

Since the dilatation of the crystal varies uniformly, this charge cannot be accounted for by expansion and it is therefore what is termed a "real" pyro-electric effect. The pyro-electric coefficient or change in surface density of charge, which is proportional to the derivative of the curves shown, evidently reverses sign just below room temperature and becomes very large. The existence of a real pyro-electric effect is of special interest because of its apparent non-existence from data obtained on other crystals.[1] It may be advisable to make a quantitative determination by some accurate method.

NEUMANN'S PRINCIPLE.

In the case of Rochelle salt the mere existence of any kind of polar effect is of great interest because of the symmetry of the crystal form. Rochelle salt is always classified as a hemihedral orthorhombic crystal. It does not have any polar symmetry in its crystal form and hence should have no directed physical properties. This conclusion is based on Neumann's principle[2] which is a very fundamental hypothesis in crystal physics. It states that the physical properties have always at least the symmetry of the crystal form. Applications of this principle are extensively used to reduce general physical formulæ to their simplest form for any particular type of crystal form.

If Rochelle salt is really in the hemihedral class of the orthorhombic system, then much of the data collected by the writer and others disprove the exactness of Neumann's principle. There are various effects so far studied that show a definite polarity in the ă crystallographic direction. In the first place there are the condenser charge and discharge throws which Anderson[1] first showed were different in the two directions, together with the unsymmetrical hysteresis loops that grew out of the writer's[2] study of Anderson's experiments. Secondly, the piezo-electric property in various electric fields shows a decided dependence on the direction of the field. Then there is also the unidirectional conductivity at some temperatures, and finally there is good evidence for the existence of a pyroelectric effect. This proves conclusively that Rochelle salt has directed electrical properties in the ă direction.

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[1] Lindemann, Ann. d. Phys., 62, No. 2, 107, 1920.

[2] Voigt, Krystallphysik, p. 3 and p. 20.

It may be that a careful study of the crystal form will show that it is not hemihedral but possibly hemimorphic and thus save Neumann's principle. All of the work done by the writer has been on material furnished by two large crystals presented by Dr. W. R. Whitney of the General Electric Company. A record of a rough crystallographic examination of the first one to be used up did not contain any reference to a polar structure. The second crystal, examined more recently, does show something that points in this direction and was not noticed at first. A drawing of the base of the crystal is shown in Fig. 1*B*. The faces indicated are all prism faces, no pyramids being present, the ends of the c axis being bounded by pinacoids. The sphenoidal faces were not present. It will be observed that the ă direction has on one side a very narrow face normal to the axis, while the other side is bounded by sloping planes. In other respects the planes occur in closed groups unless one considers the few irregularities in flatness on some of the broader faces.

If Rochelle salt is hemimorphic much of the work done on its properties will be incomplete, since all of the coefficients pertaining to any physical property would not be known. To find these would necessitate measurements in several other known directions suitably chosen with respect to the crystallographic axes. The complete set of coefficients would then appear as solutions of a set of simultaneous linear equations. The number and character of the coefficients to be determined will depend on the symmetry of the physical agency and the reaction to which it is related. These are classed by Voigt[3] as scalars, *e.g.*, temperature; vectors, *e.g.*, fields; and tensor tripels, *e.g.*, stresses or strains. Thus piezo-electric phenomena consist of relations between a tensor tripel, stress, and a vector, electric polarization. This type of relation requires in general eighteen coefficients for its complete specification. The three components of polarization are expressed by Voigt as linear functions of the six stress components as follows:

$$P_x = \delta_{11}X_x + \delta_{12}Y_y + \delta_{13}Z_z + \delta_{14}Y_z + \delta_{15}Z_x + \delta_{16}X_y, \quad \text{etc.}$$

[1] Anderson, Report to the National Research Council, Mar. and Apr., 1918.

[2] Valasek, Phys. Rev., XVII., p. 475, and XIX., p. 478.

[3] Voigt, Krystallphysik, p. 122.

In the orthorhombic system the piezo-electric moduli are reduced by Neumann's principle to the following sets:

I. Hemimorphic Group (A_z^2, E_x)

$$\begin{array}{cccccc} 0 & 0 & 0 & 0 & \delta_{15} & 0 \\ 0 & 0 & 0 & \delta_{24} & 0 & 0 \\ \delta_{31} & \delta_{32} & \delta_{33} & 0 & 0 & \delta_{36} \end{array}$$

II. Hemihedral Group (A_z^2, A_x^2)

$$\begin{array}{cccccc} 0 & 0 & 0 & \delta_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & \delta_{25} & 0 \\ 0 & 0 & 0 & 0 & 0 & \delta_{36} \end{array}$$

This brings up a consideration that places another aspect on the situation. A plate normal to the ă axis will give, in the first system above, a charge *only* when subjected to a Z_x shear. Measurements made on a plate so oriented show under a Y_z shear, the large piezo-electric effect characteristic of Rochelle salt. This seems to prove that Rochelle salt belongs to the hemihedral group since these results are in keeping with the nature of the second system of moduli given above and not in agreement with the first.

This contradictory array of facts is very puzzling, for their validity cannot be doubted. Perhaps, after all, Neumann's principle is only approximately true or probably not as general as it has been supposed to be. One may say that the crystal is made more or less polar by the physical agency applied, but this is only another way of saying that Neumann's principle is not exact or that it holds only in the limit when the stresses or fields are very small.

PIEZO-ELECTRIC THEORY.

There have been several explanations proposed for the piezo- and pyroelectric phenomena. In order to account for pyroelectricity, Lord Kelvin[1] assumed the elements of the crystal structure to be permanently polarized. Under ordinary conditions surface charges compensate for their induction at external points, but when the temperature changes the moment alters, and free charges appear on certain faces. Riecke[2] generalized this idea to account for piezo-electric phenomena as well. His "crystal molecules" consisted of rigid pole systems of specified form instead of a simple dipole. A compression or temperature change would alter the distance between them and thus change the moment and cause the appearance of charges.

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[1] W. Thomson, Phil. Mag. (5), 5, p. 26, 1878.

[2] Riecke, Nach. Ges. d. Wiss. Gott., 1891.

Later Voigt[1] modified Riecke's theory by assuming that the pole systems could be distorted. One advantage of this view is that a permanent polarization is made unnecessary. This is in better harmony with experiment. Phenomena which would accompany a high surface density of charge demanded by Riecke's theory have never been observed. Moreover, Voigt showed that the permanent polarization in tourmaline is small and equal to the pyro-electric response for a change in temperature of only 26° C. Thus he found that the permanent polarization became zero if the crystal was heated to 50° C. The writer[2] has measured the permanent polarization of Rochelle salt in the $\breve{a}$ direction and also found that it is of the order of magnitude of variations in it. It is equal to the piezo-electric excitation for one hundred grams or equal to the polarization produced by a field of only 15 volts per centimeter. Applied fields of between -1600 and $+1600$ volts per centimeter decidedly change and even reverse the direction of this polarization while they do not reverse the piezo-electric response at all. They merely change its value in such a way that it approaches zero for large fields of either sign. This shows that the changes in polarization represented by the piezo- and pyroelectric effects are not dependent on the existence of a permanent polarization.

An explanation based on different assumptions was first made by the Curie brothers[3] and developed later by Lord Kelvin.[4] The basic idea is that the crystal molecules consist of connected dissimilar parts having definite contact differences of potential. Any orderly arrangement of such rigid crystal elements connected by quasi-elastic forces acting like elastic non-conducting springs, will take on a definite charge distribution due to the contact differences of potential and depending in amount on the capacities between the various parts.

A distortion of such an arrangement will change the capacities and cause changes in the potentials of insulated plates on the faces of the crystal. Lord Kelvin points out in detail how such a mechanical model can be made to give any desired value to the twenty-one piezo- and pyroelectric coefficients and satisfy any type of crystal. A real pyroelectric effect may also be produced in this model by the distortion of certain springs by the temperature, so that even if the faces are fixed, the inner molecules rotate.

On either Riecke's or Lord Kelvin's theory, a varying piezo-electric effect such as occurs in Rochelle salt at certain temperatures would arise from a change in either the crystal structure or the forces between crystal elements. Circumstances tending to alter the grouping of these elements are known to have pronounced effects on the piezo-electric property, but such alterations in the structure in the two critical temperature ranges of Rochelle salt do not occur. For example, between − 20 and − 30° C., the piezo-electric activity decreases a thousand fold with no noticeable variation in heat absorption, dilatation, or refraction. These surely would change if the crystal form were altered.

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[1] Voigt, Nach. Ges. d. Wiss. Gott., 1893.

[2] Valasek, Phys. Rev., XVII., p. 480.

[3] J. and P. Curie, C. R., *92*, 352, 1881.

[4] W. Thomson, Phil. Mag. (5), *36*, 453, 1893.

The alternative is to suppose that the forces between crystal elements change at these temperatures. These forces are related to the cohesive forces and the elastic constants. They may vary either by changing the distances between the crystal elements or by changing their structure and hence their external field. A change in molecular structure likewise appears a little doubtful because of the constancy of the specific rotatory power. Probably this and other optical properties give no information on the piezo-electric structure because it does not involve charges with frequencies near the visible region. It appears that transformations in large ions or groups, and changes in the elastic properties of Rochelle salt occur to account for the variations in the piezo-electric activity, since these could not have been detected by the methods employed. The elastic constants await study.

If the x-ray analysis were not so difficult for this type of crystalline organic compound, it would be worth while to study the crystal structure and reflection coefficients by this means. The writer thinks that some of his previous work shows that the piezo-electric structure is intimately bound up with the water of crystallization. The place this occupies in the crystal structure and in crystal formation in general is therefore of great interest.

The writer expresses his gratitude to the National Research Council for the grant of a fellowship which enabled him to pursue this work.

Physical Laboratory,
University of Minnesota,
July, 1922.

LOW VOLTAGE ARCS IN DIATOMIC GASES.

I. Hydrogen, Nitrogen, and Iodine.

By O. S. Duffendack.

Synopsis.

Low-voltage Arcs in Hydrogen, Nitrogen, and Iodine Vapor.—After a general review of the previous experimental results and theoretical suggestions, (1) *current-voltage curves* obtained with a simple two-electrode tube are described. Precautions were taken to insure pure gases. The breaking potential was always the ionizing potential of the gas, 16.3, 16.2, and 14.6 volts, respectively, for the three gases. The striking potential was greater than the breaking one by an amount which increased with the pressure and with increasing cathode filament temperature. *In dissociated hydrogen*, maintained at a high temperature within a thin tungsten cylinder heated electrically, an arc was readily maintained at the ionizing potential of the atom, 13.7 volts, and under very favorable conditions, at the radiating potential, 10.0 volts. *In dissociated iodine vapor*, the arc was maintained at 12.1 volts and under certain conditions at the ionizing potential, 10.2 volts. Nitrogen was not appreciably dissociated in the furnace. *The critical potentials* given above agree with the best previous results within ± 0.2 volt as a rule. Those associated with the atom are experimentally distinguished from those associated with the molecule.

Electric Furnace Spectra of Hydrogen, Nitrogen and Iodine to 2500° C.—In hydrogen, the series lines flashed in when the arc was struck, even as low as 10.6 volts, but the bands did not appear. Evidently the series lines are due to the atom and the bands to the molecule. In nitrogen, a brilliant "flare" was produced at potentials which decreased from 70 to 40 volts as the temperature was increased. This "flare" shows both the positive and negative bands along with the spectrum of tungsten; it is probably due to the formation of "active" nitrogen. At 70 volts the first lines, 5006 and 5003 Å., appeared, and at 90 volts only two more, 5680 and 5667 Å. Reasons are given for assigning the positive bands to the neutral molecule, the negative bands to the ionized molecule and the lines to the atom. In iodine, the arc lines, particularly 4860 Å., flashed in when the arc struck, the enhanced lines coming in at higher voltages. No band spectrum appeared.

New negative bands of nitrogen were found at 5075, 5018 and 4961 Å.

General Theory of Low Voltage Arcs.

THIS investigation was undertaken to see if additional light could be obtained by this method upon the critical potentials of diatomic gases; to study the effect of the dissociation of a gas upon the potentials at which an arc will strike and break; and to investigate, incidentally, the excitation of the spectra of the substances.

The method of investigating critical potentials by means of low voltage arcs differs from the methods usually employed for determining ionizing and radiating potentials in that very much greater electron streams are passed through the gas and the gas is usually at a considerably greater pressure. Up to the time this investigation was begun this method had been employed only with monatomic gases and vapors. Some seeming disagreements appeared between the results obtained by means of low voltage arcs and those by the usual methods. When only a moderately dense electron stream was sent through a gas, the arc would strike at the ionizing potential as determined by the usual methods, but when a dense electron stream was employed the arc could be made to strike as low as the radiating potential. The striking of an arc indicates that considerable ionization is taking place, and this is confirmed by the appearance of the spectrum of the substance. As Bohr's theory indicates that the atom is not ionized at the radiating potential, and as the usual methods often indicate the absence of ionization, the striking of the arc at this potential appeared to be in conflict with the previous results.

Various explanations of these anomalous effects with dense electron streams have been proposed. In some cases it was thought that the ionization of impurities present might account for the effect, and McLennan[1] attributed the appearance of "faint arcs" to electrons of abnormally high velocities in the electron stream. These explanations seemed insufficient in most cases and others were proposed. Millikan[2] suggested that the radiation produced by impacts at the radiating potential might act photoelectrically upon the atoms of the filament or of the gas and thus produce additional electrons which would in turn be accelerated by the applied field and make impacts at the radiating potential and so there would be a multiplication of the original current. Richardson and Bazzoni[3] and Van der Bijl[4] put forward the theory of successive impacts, and the former also suggested that a combined action of radiation and of impacts accounts for the ionization. K. T. Compton[5] investigated the adequacy of the theory of successive impacts and concluded that, while it is an important factor, in general, ionization produced in this way is insufficient to account for the observed results. He has recently shown[6] that the cumulative effect of absorbed radiation is far more effective than successive impacts, and it seems that this may account for most of the cases reported.

In order to understand better the results obtained, it will be well for us to recall what is meant by an arc. Richardson has shown that the saturation thermionic current from an incandescent cathode is given by

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[1] Proc. London Phys. Soc., 31, 1 (1918).

[2] PHYSICAL REVIEW, 9, 378 (1917).

[3] Nature, 48, 5 (1916).

[4] PHYS. REV., 10, 546 (1917).

[5] PHYS. REV., 15, 130, 476 (1920).

[6] Amer. Phys. Soc. Proc., New York meeting, 1922.

$$i = aT^2\epsilon^{-\frac{b}{T}}$$

where a and b are constants and T is the absolute temperature of the filament. When this equation is tested, however, it is found that, while it holds quite well at the lower temperatures, the current falls short of the value predicted by the equation for the higher temperatures and reaches a maximum value which is much less than the saturation current. The point of departure from the Richardson relation depends upon the voltage applied and is earlier for the lower voltages. The maximum current obtainable is likewise less the lower the voltage.

The reason for the failure of Richardson's equation was investigated by Langmuir,[1] and it was found to be due to the effect of the space charge of the emitted electrons. If no electrons are emitted by the filament, the potential will vary linearly between the electrodes. When electrons are emitted and, under the influence of the field, pass over to the anode, they form an electric current and build up a space charge. The potential gradient will no longer be uniform between the electrodes but will be less near the filament on account of the concentration of electrons there. These electrons will repel one another and so will impede those just being emitted by the filament. As the speed of an electron is proportional to the potential gradient, there will be a diminution of the average velocities of the electrons near the filament and a resulting increase in concentration. This results in increased impedance until finally the space charge becomes so great that the potential gradient becomes zero or even negative. An equilibrium condition will be reached in which the electrons emitted with velocity components parallel to the electric intensity below a certain amount will be stopped and driven back to the filament. There can then be no further increase in current at the prevailing temperature of filament and potential applied.

Now if ionization takes place, we have a quite different state of affairs. The positive ions will neutralize the space charge of the electrons. The densities of electrons and of ions, and hence the space charges due to them, will vary inversely with their velocities. Their velocities vary directly as their mean free paths and inversely as the square roots of their respective masses. Thus each positive ion neutralizes the space charge of $4\sqrt{2}\sqrt{1846\,M}$ electrons, where M is the molecular weight.[2] Therefore, one positively charged hydrogen atom will neutralize the space charge of 243 electrons, one positively charged hydrogen molecule will neutralize 343 electrons. Now if we have reached the maximum current limited by the space charge, the formation of one positive hydrogen molecule ion will permit the emission of 342 additional electrons. If every electron emitted ionized a molecule, the electron current would increase more than three hundred times. These newly emitted electrons would in their turn be accelerated and would ionize other molecules, and so on, and the current would continue to increase until the saturation current indicated by Richardson's equation is reached. To this current would be added the current carried by the ions and electrons formed in the process of ionization. There would be a further increase in emission due to the heating of the filament as a result of its bombardment by positive ions, and there would be a diminution of current due to the recombination of ions and electrons. The data from hydrogen show ratios of current in the arc to that before the arc of from 2 to 120 depending upon the temperature of the filament. The current through the arc was about that to be expected from Richardson's equation.

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[1] Phys. Rev., 2, 543 (1913).

[2] The factor 4 is due to the negligible size of the electron and the factor $\sqrt{2}$ to the fact that its speed is of a higher order than that of the molecules among which it moves. See any treatise on Kinetic Theory.

Now let us look a little further into the mechanism of the arc. When the space charge immediately surrounding the filament is neutralized or reversed by positive ions, we will have a large increase in electron emission from the filament, and the arc will strike. This is accompanied by a redistribution of the electric intensity in the tube, resulting in a large drop in potential near the cathode. This fall in potential will be a large fraction of the total potential difference between the electrodes, but, obviously, the potential can nowhere be higher than at the anode as this would give a negative gradient and would prevent electrons which had lost their velocities from reaching the anode. The exact distribution of potential cannot be computed for want of knowledge concerning the distribution of space charges. This cathode fall of potential will enable electrons to ionize at their first impact, or, at least, it will greatly increase the ionization near the cathode. This view of the distribution of electric intensity in the arc is supported by the observations that the spectrum is most intense in the region near the filament and that the glow of the arc, if it is small, is confined to the region immediately surrounding the filament.

If we assume the distribution of electric intensity explained in the preceding paragraph, the potentials at which an arc will strike and break can easily be deduced. As the striking of the arc follows the neutralization of the space charge, it will normally occur at or above the ionizing potential of the substance, depending upon the temperature of the filament and the pressure of the gas. If a considerable fraction of the molecules are in a partially ionized condition, due to the absorption of a quantum of radiation or to an impact with an electron possessing sufficient energy to displace an electron in the molecule but not to remove it, a sufficient number of positive ions may be formed by impacts with these molecules to cause the arc to strike at a potential below the ionizing potential. As it seems improbable from Professor Compton's[1] work that this can be accomplished by successive impacts alone, we need examine only the case of the absorption of radiation. If, as is usually the case, the radiation comes from the substance itself and not from without, electron impacts at the radiating potential will be required to produce the radiation, as radiation corresponding to the first line of the principal series is necessary. Therefore, it is possible to get an arc to strike at a potential equal to the difference between the ionizing and radiating potentials of the substance, provided that this difference is not less than the radiating potential; or at the radiating potential, provided that this is not less than half the ionizing potential. With dense electron streams, the arc has been made to strike in all of the monatomic gases thus far investigated at the radiating potential. It is noteworthy, however, that a distinct time lag in the striking of the arc was noted by nearly all of the observers for voltages between the radiating and ionizing potentials. It was found impossible to get the arc to strike in the diatomic gases investigated at a voltage less than the ionizing potential. This is probably due to the loss of energy by inelastic impacts in the diatomic gases and to the fact that the molecules are unable to absorb and reëmit the resonance radiation, which comes from the atoms.

After the arc has struck, it will continue as long as the space charge surrounding the filament remains positive. With a dense electron stream the arc can be maintained indefinitely at the radiating potential in a monatomic gas, provided that this is not less than half the ionizing potential. Obviously, the arc can be maintained temporarily at a voltage equal to the difference between the ionizing and radiating potentials even when this is less than the radiating potential, but it must eventually break due to the loss of radiation from the tube.

In diatomic gases the arc invariably broke at the ionizing potential, but it is comparatively easy to maintain the arc in monatomic gases at the radiating potential when this is not less than half the ionizing potential. In some cases the arc has been maintained for a considerable time at the radiating potential, or less, even when this is less than half the ionizing potential. This was done in the case of mercury vapor by Hebb,[2]

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[1] Loc. cit.

[2] Phys. Rev., 9, 371 (1917); 12, 482 (1918).

Millikan,[1] and Compton and Yao;[2] in sodium vapor by Wood and Okano,[3] and in mixtures of sodium and mercury and potassium and mercury vapors by Hebb. That these are not anomalous cases was shown by Compton and Yao, who worked out a satisfactory explanation of these cases upon the basis of the distribution of velocities of emission of the electrons. The ionizing potential of mercury is 10.4 volts and the radiating potential is 4.9 volts. Compton and Yao maintained the arc in mercury vapor at 1.8 volts. They showed that there are a sufficient number of electrons emitted from a hot filament with initial velocities sufficient to make up the difference between the 1.8 volts observed and the 5.5 volts theoretically required to maintain the arc.

The case of helium is a more striking one. The ionizing potential of helium is 25.5 volts and radiating potentials of 20.4 and 21.2 volts have been found. It should, therefore, be possible to maintain an arc in helium temporarily at 5.1 or 4.3 volts. Kannenstine[4] got evidence that this can be done by taking oscillograph records of the current through a helium arc when an alternating field is applied. These records show a persistence of the arc at about 4 volts when a sixty-cycle circuit was used. This would give a time interval of the order of a hundredth of a second. Compton, Olmstead, and Lilly,[5] maintained an arc for a considerable time at 8 volts, and Miss Davies's [6] work indicates that the arc can be maintained for an indefinite period at 13 volts. These observers do not claim that these voltages are critical potentials; the important point is that in the case of helium it seems possible to maintain an arc indefinitely at a potential far too much below the radiating potential to allow an explanation on the basis of velocity distribution. Miss Davies suggest that helium is converted into a metastable form by electron impacts at 20.4 volts and that this is then ionized by impacts of 5.1 volts or more. When these ions are neutralized the atom remains in the metastable condition and does not return to the normal form. Once this is formed, then, the arc can be maintained at a potential as low as 5.1 volts until the helium is reconverted into the normal form. The process by which the metastable atom is changed into the normal atom is not well understood, although Franck and Knipping[7] suggest that it depends upon the catalytic action of impurities. It should be noted that the arc does not strike in helium at potentials less than 20.4 volts.

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[1] PHYS. REV., 9, 378 (1917).

[2] Amer. Phys. Soc. Proc., Washington meeting, 1922.

[3] Phil. Mag., 34, 177 (1917).

[4] Amer. Phys. Soc. Proc., New York and Washington meetings, 1922.

[5] PHYS. REV., 15, 545 (1920).

[6] Roy. Soc. Proc., A, 100, 599 (1922).

[7] Zeit. für Physik, 1, 320 (1920).

Apparatus.

The apparatus employed in this investigation was of two types. The first was a simple two-element tube, consisting of a tungsten wire filament and a nickel plate anode placed at a distance of about 5 mm. from the filament. A potential difference was applied between the negative end of the filament and the plate and could be varied by control rheostats. The current between the electrodes was read on a sensitive milliammeter placed in series with the arc. The current through the arc was recorded as the voltage was raised by steps from zero. The striking of the arc was indicated by a sudden jump in the current and also usually by the appearance of a glow around the filament and the flashing in of the spectrum of the gas. The potential across the arc was corrected to that which obtained between the middle of the filament and the plate by subtracting from the reading of the voltmeter half the potential drop across the filament. This correction is subject to error when the filament is very hot as there may then be sufficient emission from the negative end of the filament to maintain the arc. The effect of initial velocities of emission from the filament is such as to more or less counterbalance this error.

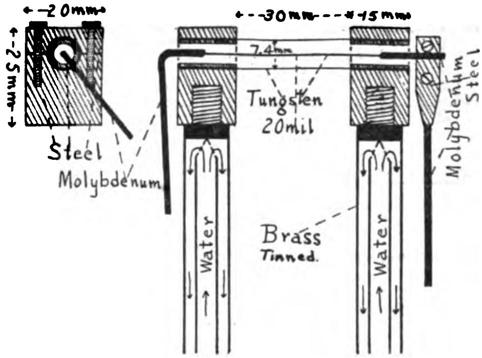

Fig. 1.

It was found impossible in the simple tube to maintain the arc at voltages less than the ionizing potential. The failure to do so was ascribed to there being an insufficient amount of the monatomic gas present in the tube when due only to the dissociating action of the filament and of the arc. Professor Compton suggested that it might be possible to dissociate hydrogen and other gases by means of a tungsten furnace which could also be used as one of the electrodes of the arc. The construction of the furnace developed by the writer is shown in the accompanying diagram. It consists of a cylinder of very thin sheet tungsten mounted on water cooled leads. A tungsten filament ran axially through the cylinder and was made the cathode. The fall of potential in the furnace and that in the filament were in the same direction. In the earlier experiments with this tube, the potential was applied between the positive end of the furnace and the negative end of the filament. The reading of the voltmeter was corrected to give the potential between the middle of the electrodes by subtracting half the sum of the voltage drops across the furnace and the filament. This correction was checked by a sharp rise in the thermionic current when the voltmeter read this amount. This correction is subject to the same error as in the case of the simple tube for very hot filaments. The parts of the furnace were later modified so that the drops of potential in the furnace and in the filament and also in the furnace leads and filament leads were identical. The potential was then applied between the negative ends of the furnace and filament and the voltmeter read the voltage obtaining between corresponding parts of the furnace and the filament.

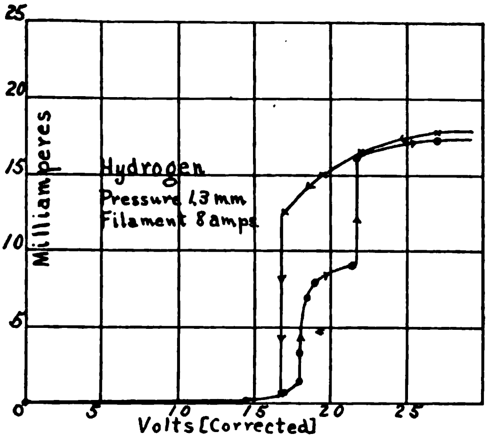

Fig. 2.

This condition was practically equivalent to having two equipotential surfaces as electrodes. The temperature of the furnace was estimated from the resistivity of the tungsten. Calculations of the resistivity showed that temperatures of about 2,500° C. were obtained.

Arcs in Hydrogen.

The hydrogen was generated by the electrolysis of dilute sulphuric acid and was purified by passing it over phosphorous pentoxide and through charcoal immersed in liquid air. The pressure of the gas in the tube was read on a McLeod gauge. Before the gas was admitted into the tube, the electrodes were thoroughly glowed out, and when the simple tube was used, it was thoroughly baked.

Figs. 2, 3, and 4 show the effect of the temperature of the filament on the potential at which the arc strikes and breaks. These curves were obtained from three successive runs in hydrogen at a pressure of 1.3 mm. The potential of the break is lower the greater the filament current, becoming slightly less, Fig. 4, than the ionizing potential of hydrogen. This illustrates the error in the zero correction for hot filaments as pointed out in a foregoing paragraph.

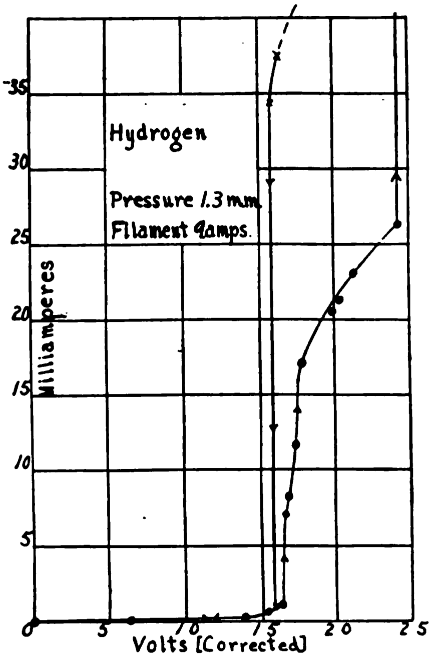

Fig. 3.

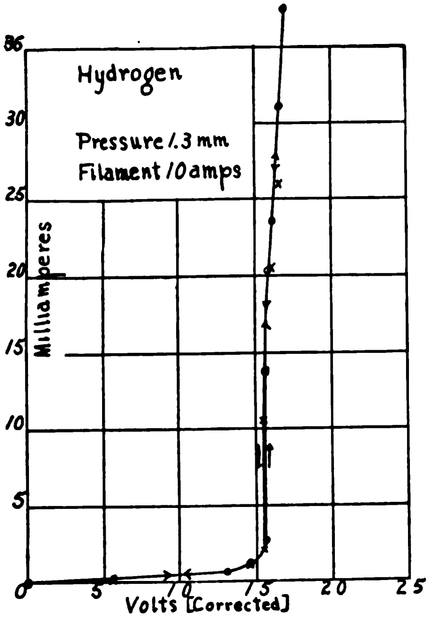

Fig. 4.

Figs. 5, 6, and 7 show the effect of the pressure of the gas upon the potentials at which the arc strikes and breaks. For these curves runs were taken at pressures of 0.4, 2.4 and 5.5 mm. and the filament currents were such as to give practically the same increase in current when the arc struck. The striking potential regularly increases with the pressure as does the difference between the striking and breaking potentials. The curves indicate that there is an optimum pressure at which the arc can be maintained to the ionizing potential of the gas with a moderately hot filament.

At pressures above about 0.5 mm. ionization sets in at the ionizing potential as is indicated in Figs. 2, 3, 6 and 7, but, though there may be a large increase in current, the arc does not strike until the voltage is raised considerably above the ionizing potential, the amount depending upon the pressure of the gas and the temperature of the filament. If the applied potential is decreased before the arc strikes, the curve is retraced, but after the arc strikes, the current remains at a higher value until the arc breaks. Before the arc strikes, the current seems to approach a saturation value as in the case of thermionic currents in high vacua. This is probably due to a gradual shifting of the region of predominately positive space charge toward the filament. A large fraction of the potential difference applied to the electrodes is used up between the filament and the boundary of the region of positive space charge, and so the electrons enter this region at approximately their maximum speeds, the actual speed depending upon the potential and upon energy losses by inelastic impacts. The energy losses by inelastic impacts are greater for the higher pressures due to the increased number of collisions, and so the potential difference required to be applied to cause an electron to enter the region of positive space charge with sufficient energy to ionize upon impact will be greater the greater the pressure of the gas. This accounts for the increase in the striking potential with the pressure. Now, after this region of positive space charge has reached a certain thickness, a further increase in thickness will not greatly increase the probability that an electron entering this region with energy sufficient to ionize a molecule will make an ionizing impact. There will then be very little increase in current until the space charge immediately surrounding the filament becomes positive, and the arc strikes. After the

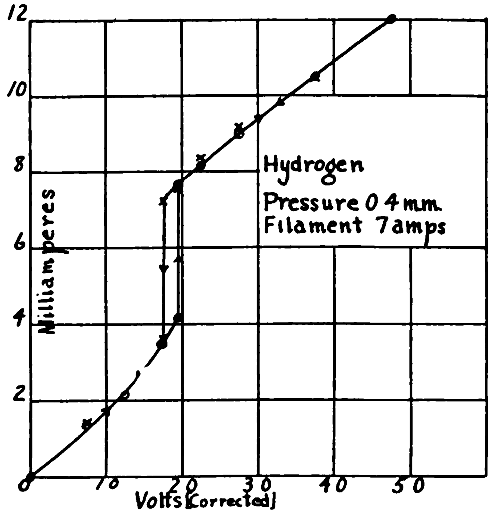

Fig. 5.

apparent saturation current has been reached, a slight change in the conditions in the tube or a slight shifting of the space charges will cause the arc to strike, and so the striking of the arc may vary by several volts for the same pressure and filament current.

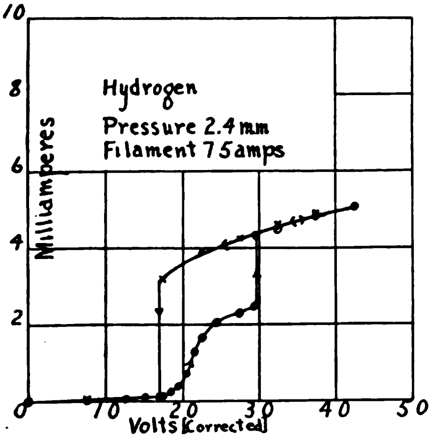

Fig. 6.

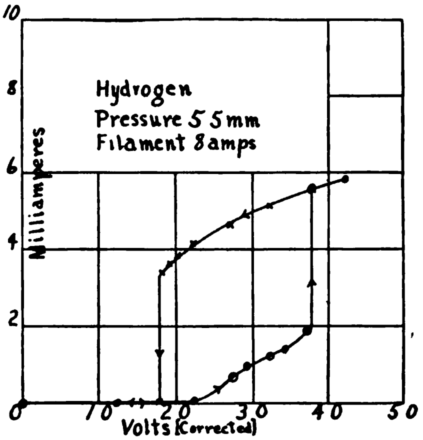

Fig. 7.

In this type of apparatus the potential of the break of the arc was far more constant than that of the strike. For pressures between 0.85 mm. and 3 mm. and with moderately hot filaments the breaks were remarkably constant, having a mean deviation from the average of 0.3 volt. The average of fourteen runs at these pressures gives a breaking potential of 16.35 volts which is within the range of the values of the ionizing potential of hydrogen reported by various observers.

As Bohr's theory puts the ionization potential of the hydrogen atom at 13.52 volts, calculated from the convergence frequency of the Lyman series, and the radiating potential at 10.14 volts, it should be possible to maintain the arc at these potentials if a sufficient amount of monatomic hydrogen could be obtained. The tungsten furnace was designed to dissociate the gas by means of high temperatures. The amount of dissociation to be expected was calculated by means of Nernst's equation of the "reaction-isobar,"

$$\log \frac{x^2}{1 - x} P = - \frac{Q_0}{4.571\, T} + 1.75 \log T - \frac{\beta}{4.571} T + \sum \nu C.$$

x = the fraction of the molecules present which are monatomic,
P = the total pressure,
Q_0 = the heat of dissociation at absolute zero,
T = the absolute temperature,
β is a constant depending upon the rate of change of the specific heat with the temperature,

4.571 is the gas constant per gram mol. times the logarithmic modulus,

C is Nernst's chemical constant.

Q_1 can be calculated from Q, the heat of dissociation at ordinary temperatures, by means of the formula: $Q=Q_1+\alpha T+\beta T^2+$ etc., where α = specific heat.

Taking the heat of dissociation, Q, to be 84,000 calories per gram-molecule, $\beta = 0.000225$, and the chemical constants for diatomic and monatomic hydrogen to be[1] − 3.4 and − 1.6 respectively, the percentages of monatomic hydrogen in equilibrium with diatomic hydrogen at various temperatures and pressures are indicated in the following table:

Pressure.	1000° K.	1500° K.	2000° K.	2500° K.	3000° K.
0.5 mm....	.005	2.36	61.5	Complete	
1.0 mm....	.004	1.69	49.5	98.8	
5.0 mm....	.002	0.74	26.7	90.4	Dissociation

When the furnace was not heated, the arc struck and broke at the ionizing potential of the molecule, and there was no evidence of ionization below about 16 volts. With the furnace hot, considerable ionization was produced at about 10 volts and 13.5 volts as is indicated by the

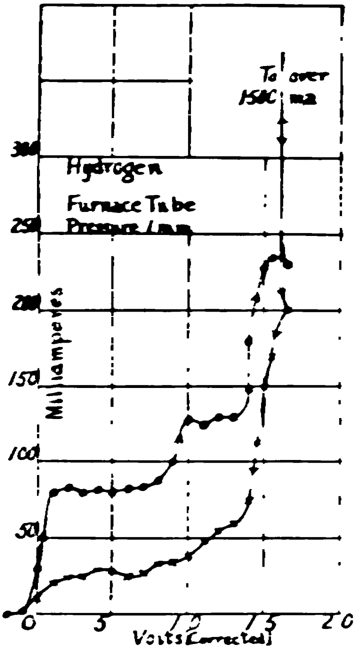

Fig. 8.

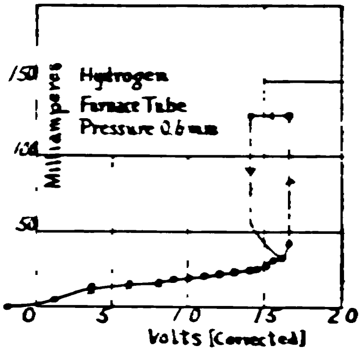

Fig. 9.

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[1] Reiche, Ann. d Physik, 58, p. 657, 1919 and Schames, Phys. Zeit., 21, p. 41, 1920.

curve for the thermionic current, Fig. 8. Later a temperature was reached at which the arc struck at the ionizing potential of the molecule and was maintained to the ionizing potential of the atom, Fig. 9, indicating that the increase in dissociation in the arc enabled it to be maintained in monatomic hydrogen. Finally, practically complete dissociation was obtained; the arc struck easily at the ionizing potential of the atom, and the curve shows no indication of a further increase in ionization at the ionizing potential of the molecule, Fig. 10(*b*). With a very hot furnace and a large electron emission the arc was made to strike at 10.6 volts, Fig. 10(*a*) which is very near the radiating potential of the atom, and no further discontinuities were observed at higher voltages. It was quite difficult to do this and it was only done when the furnace had not been maintained at the high temperature for a long time. The curve 10(*a*) was drawn from memory. This striking of the arc was repeated several times and the potential and current noted, but an accident prevented a run being made with the current and voltage recorded by steps. The failure to get the arc to strike at potentials lower than 13.5 volts later was attributed to impurities coming from the walls of the tube and from the clamps and leads when they became warm. As the furnace was mounted on water-cooled leads, the tube had to be put together with Khotinsky cement and so it could not be baked out.

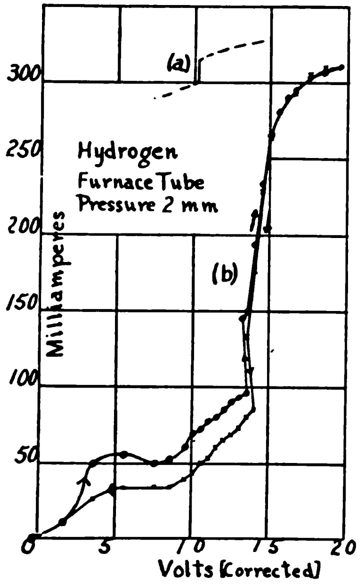

Fig. 10.

This is the first experiment of this kind performed in an atmosphere of atomic hydrogen, and these results constitute, it is believed, the first direct experimental proof of the correctness of the values of the radiating and ionizing potentials predicted by Bohr's theory for the *hydrogen atom* and of the interpretation of the ionizing potential of the molecule as due to its dissociation plus the ionization of one of the atoms.

Table I. gives the critical potentials of hydrogen predicted by Bohr's theory together with the average break points obtained in this investigation and the critical potentials reported by various observers. The heat of dissociation was calculated in each case by subtracting the thirteen-volt break from the sixteen-volt break when ionization was reported in

TABLE I.

Bohr's Theory.	This Investigation.	Franck, Knipping & Kruger.[1]	Davis & Goucher.	Horton & Davies.[2]	Compton & Olmstead.[4]	(Mohler & Foote)[5] Foote, Mohler & Kurth.[6]	Boucher.[7]
29.74 *D*+2*I*		30.45 *D*+2*I*					
26.36 *D*+*I*+*R*							
22.98 *D*+2*R*							
						(16.5 *I'*)	
16.22 *D*+*I*	16.35 *D*+*I*	17.1 *D*+*I*	15.8 *I*	16.9 *I*	15.9 *D*+*I*	16.0 *I*	15.6 *I*
				14.4 *I*			
13.52 *I*	13.7 *I*	13.6 *D*+*R*	13.6 *R*	13.9 *R*	13.4 *I*	(13.3 *I'*)	13.6 *I*
						(12.2 *R*)	
12.84 *D*+*R*						11.8 *R*	
		11.5 *I*(Mol)				10.5 *R*	
10.14 *R*	10. *R*		11. *R*, *I'*	10.5 *R*	10.8 *R*, *I'*	(10.4 *R*)	10.1 *R*
						(3.2 *D*)	
2.7 *D*	2.55 *D*	3.5 *D*		2.5 *D*	2.5 *D*	2.7 *D*	2.0 *D*

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[1] Verhand. d Deutsch. Phys. Ges., 21, 728 (1919).

[2] Phys. Rev., 10, 101 (1917).

[3] Roy. Soc. Proc., A, 97, 23 (1920).

[4] Phys. Rev., 17, 45 (1921).

[5] Jour. Optical Soc. Amer., 4, 49 (1920). Bureau Standards, 1920, 670.

[6] Amer. Phys. Soc. Proc., Toronto Meeting, Dec., 1921.

[7] Phys. Rev., 19, p. 189, 1922.

both cases. The heat of dissociation was measured by Langmuir[1] who found it to be equivalent to 3.6 volts.

It was not the purpose of this investigation to determine accurately the critical potentials of the gases studied, and no great degree of accuracy is claimed for the potentials reported. The purpose of this investigation was to interpret and not to determine critical potentials.

Spectroscopic Observations on Hydrogen.

A systematic study of the excitation of the spectrum of hydrogen was made during the investigation of the arcing characteristics. A Hilger direct-reading spectroscope was used and visual observations were made.

With the two-element tube, the lines and bands flashed in when the arc struck and disappeared when the arc broke. All of the bands observed belong to Group I. of Fulcher's[2] classification as far as his classification extends and were of those for which Dufour found no Zeeman effect. The observations were made for potentials up to 40 volts which probably accounts for the fact that none of the bands of Group II. were observed, except that one member of each of the two pairs of bands which were placed in both groups was observed. The bands of Group II. are those which increase in intensity with the voltage and include those which Dufour found to show the Zeeman effect.

In the tungsten furnace, the lines flashed in when the arc struck, as low as 10.6 volts, and were strongly reversed in the intense arc of the furnace. The bands did not appear when the furnace was hot and the gas was practically completely dissociated. This is additional evidence that the line spectrum is due to the atom and the band spectrum to the molecule and is in agreement with the conclusions of G. P. Thomson[3] as a result of an investigation of the spectrum emitted by positive rays in hydrogen.

Fulcher's work shows that there are at least two groups of bands in the second spectrum of hydrogen, and Merton[4] suggests that there are three. There are several possible explanations for the different kinds of bands; all of them attributing the radiation to the molecule, as follows: One, or both, of the electrons of a neutral molecule may be set radiating as a result of their disturbance by an electron impact which does not dissociate or ionize the molecule, or by the recombination of an electron with an ionized molecule, or by the recombination of two neutral atoms. It is by the recombination of neutral atoms that Strutt suggests the glow of active nitrogen is produced. The remaining electron of an ionized molecule may be set radiating as a result of its disturbance by an electron impact which does not produce dissociation, or by the union of a neutral atom and an ionized atom. There was no means of testing any of these proposed explanations from the data of the investigations reported. I merely wish to point out that there are possible mechanisms for the radiation of several kinds of bands by the hydrogen molecule. The H_3 molecule, which is often present in positive rays in hydrogen, offers additional possibilities for band spectra, and Wendt and Landauer[2] suggest that it may be the source of the bands observed by them.

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[1] Langmuir, Irving, Amer. Chem. Soc. Jour., 34, p. 860, 1912, and 37, p. 417, 1915.

[2] Astrophysical Journal, 37, p. 65, 1913.

[3] Phil. Mag., 40, p. 240, 1920.

[4] Royal Society Proc., A, 96, 382, 1919.

ARCS IN NITROGEN.

Nitrogen was generated by the reaction of sodium nitrite and ammonium chloride. It was passed through a tube of hot copper turnings and collected over distilled water. Before being admitted into the experimental tube it was passed over phosphorous pentoxide and through a tube immersed in liquid air.

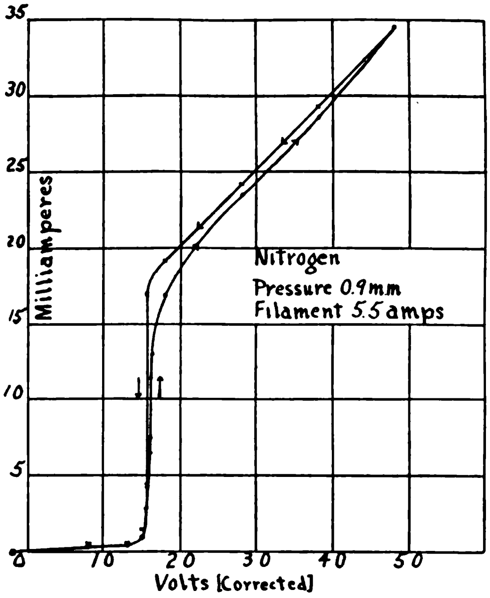

Fig. 11.

The curves obtained for nitrogen, Figs. 11 and 12, are similar in most respects to those for hydrogen when the simple tube was used. The striking potential was higher than the ionizing potential for high gas pressures, but there was less definite evidence of an apparent saturation current before the arc struck. The difference between the striking and breaking potentials was less in nitrogen than in hydrogen for the same mean free path of electrons. These differences are probably due to the greater elasticity of impact and consequently to the greater space charge in hydrogen than in nitrogen, combined with the greater effectiveness of nitrogen positive ions in neutralizing the space charge of electrons. The current continues to increase quite rapidly with the voltage after

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[2] Amer. Chem. Soc. Jour., 44, 510, 1922.

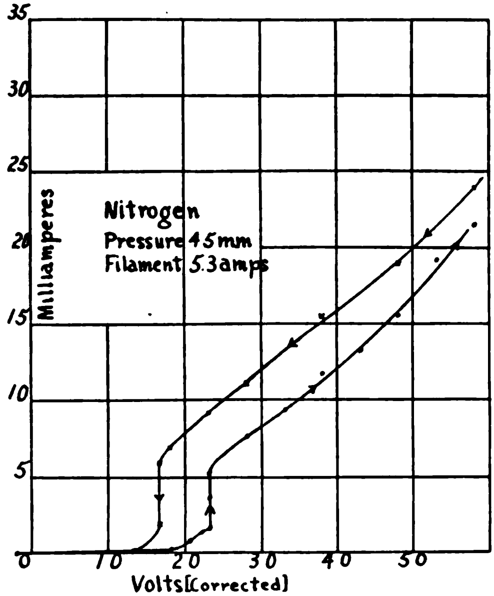

Fig. 12.

TABLE II.

	Davis & Goucher.[1]	Smyth.[2]	Found.[3]	Mohler & Foote.[4]	Stead & Gosling.[5]	Brandt.[6]	Boucher.[7]
Resonance Potentials	7.5 9.0	6.29 7.3 8.29		8.18		7, 8.5	8.4
Ionization Potentials	18	18	15.8	16.9	17.2	17.75	15.8

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[1] Phys. Rev., 13, 1 (1919).

[2] Phys. Rev., 14, p. 409 (1919).

[3] Phys. Rev., 16, p. 41 (1920).

[4] Jour. Optical Soc. of Amer., 4, p. 49 (1920).

[5] Phil. Mag., 40, p. 413 (1920).

[6] Zeit. für Phys., 8, p. 32 (1921).

[7] Phys. Rev., 19, p. 189 (1922).

the arc has set in, while in hydrogen the current did not increase much after the arc had struck. It was impossible to maintain the arc at potentials lower than the ionizing potential, and the average of the break points was 16.15 volts, which is within the range of ionization potentials reported for nitrogen as shown in Table II.

It was impossible to maintain the arc at lower potentials in the tungsten furnace and so it was concluded that the degree of dissociation of nitrogen at the temperature of the furnace was small. This is in agreement with the conclusion reached by Langmuir[1] for the heat of dissociation of nitrogen.

When the filament was quite hot, the conductivity of the arc increased very rapidly for voltages of 70 volts or more, and, with no further change in the control rheostats, the current increased enormously while the voltage decreased and the arc turned into a brilliant "flare." When the rheostat was operated so as to normally increase the potential across the arc, the voltage decreased instead and the current increased. In this manner a current of more than 15 amperes was obtained at a voltage of about 25 volts. There was a rapid wasting of the tungsten filament in the flare and the nickel anode and the leads supporting the filament were usually quickly melted. By using a tungsten anode and five tungsten filaments in parallel, the flare was maintained for a considerable time and its spectrum studied. Besides the spectrum of nitrogen, the spectrum of tungsten showed up strongly. A black deposit accumulated on the walls of the tube which appeared to be tungsten nitride. The wasting of the filament was not sufficiently rapid to justify the conclusion that the arc was now maintained in tungsten vapor, and so a more probable explanation was sought.

As the conditions in the arc are similar to those in a condensed discharge in a vacuum tube, it was concluded that "active" nitrogen was formed. The excitation of the tungsten spectrum was, then, analogous to the excitation of the spectra of hot metals in "active" nitrogen as accomplished by Strutt,[2] and it was explained by him to be due to the burning of the metals in this nitrogen. He found that this glowing nitrogen has a high electric conductivity, comparable to that of salts in a Bunsen flame, and so this accounts for the increased conductivity of the arc in the "flare." This explanation of the production of the "flare" probably also accounts for the anomalous thermionic emission of tungsten filaments in nitrogen for potentials above 75 volts as discovered by Langmuir.[3]

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[1] Amer. Chem. Soc. Jour., 34, 860 (1919).

[2] Royal Soc. Proc., A, 85, p. 219 (1911) et seq.

[3] PHYS. REV., 2, p. 450 (1913).

Strutt concluded that "active" nitrogen is simply monatomic nitrogen and results from the dissociation of nitrogen in the electric discharge. It was possible to get the "flare" in a hot tungsten furnace at a somewhat lower voltage than in the simple tube, *i.e.*, as low as 40 volts instead of 70, and this may be accounted for on this assumption, by a slight increase in dissociation due to the temperature of the furnace. This is the only evidence obtained that there was any dissociation of nitrogen by thermal action.

SPECTROSCOPIC OBSERVATIONS ON NITROGEN.

Nitrogen has a rich line spectrum and a very complicated band spectrum. The band spectrum has been classified by Deslandres[1] into three positive band spectra and a negative band spectrum. The first positive bands came in with the arc and increased slightly in intensity with the voltage. They have been excited in various ways by slow cathode and canal rays. The second positive bands came in with the arc and decreased in intensity with increased voltage as has also been observed by Fulcher.[2] These bands disappear as the potential is increased, but reappear in the "flare" along with the spectrum of tungsten.

This reappearance can be accounted for on the basis of the explanation of the "flare" as given above, for these bands were found by Fowler and Strutt[3] to be invariably present in the spectrum of the nitrogen afterglow. Besides the second positive bands they find also the first positive bands, with certain groups greatly enhanced, and the third positive bands in the afterglow. They concluded that "active" nitrogen was simply monatomic nitrogen and that the glow was produced by the reunion of the atoms. This manner of excitation corresponds in energy to electron impacts at quite low potentials, very probably less than the ionizing potential.

L. and E. Bloch[4] photographed one of the ultraviolet bands of the second group at 12 volts, which is considerably under the ionizing potential of nitrogen. Erich Brandt[5] by using a four-element tube and varying the potential by intervals of 0.05 volt got a series of discontinuities in the galvanometer current for voltages between 7.5 and 8.2 volts. By applying the $h\nu$ relation to these discontinuities he constructed a band which agrees in frequency difference with some of the positive bands. He found this band characteristic of these discontinuities to persist beyond the ionizing potential and concluded that the nitrogen molecule is ionized without dissociation. A survey of the various ways in which the positive bands are excited indicates that they can all be excited at less than the ionizing potential and so must be due to the neutral molecule.

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[1] Comptes Rendus, 101, p. 1256, 1885 et seq.

[2] Astrophys. Jour., 37, p. 60 (1913).

[3] Roy. Soc. Proc., A, 85, p. 377 (1911).

[4] Comptes Rendus, 170, p. 1380 (1920).

[5] Zeit. für Phys., 8, p. 32 (1921).

The negative bands appear a volt or two above the ionizing potential and increase markedly in intensity with the voltage. Three bands not previously reported were observed at 5075, 5018 and 4961 Å. in good agreement with their calculated positions. The negative bands appear intensely only in regions of strong ionization and positive space charge and must, therefore, be due to the ionized molecule.

At about 70 volts the green doublet 5006, 5003 of the line spectrum appeared faintly and increased in intensity with the voltage. At 90 volts it was quite strong and the yellow lines 5680 and 5667 were also seen. None of the other strong lines were observed although the regions in which they lie were thoroughly searched.

It is difficult to account for the non-appearance of the line spectrum even in the "flare" at potentials less than 70 volts. It may be impossible to dissociate the molecule and ionize one of the atoms at a single impact. Sir J. J. Thomson,[1] from a consideration of the Doppler shifts of the lines in positive rays in nitrogen, concluded that some of the lines, the line 5003 being one of them, are due to the double ionization of the atom and are therefore enhanced lines. This accounts for the high potential required for the excitation of some of the lines but does not explain why so few lines appeared. Perhaps a grouping of the lines in series will clear the matter up. A more complete discussion of the excitation of the spectrum of nitrogen will be published in the Astrophysical Journal.

ARCS IN IODINE.

Chemically pure iodine was resublimed into a bulb having a thin wall. The distilling apparatus was kept connected to a diffusion pump through two liquid air traps, and the sublimation was carried on at a very low pressure. After a sufficient amount had been condensed, the tube was sealed off under a vacuum and then sealed into a second bulb which was connected to the experimental tube. After all the parts had been heated to clean up the surfaces, the iodine was liberated by breaking the thin-walled bulb by means of an iron weight lifted by a magnet.

The vapor pressure of the iodine in the experimental tube was controlled by means of a water bath. When the simple tube was employed, the tube containing the iodine was kept at the temperature at which iodine has the vapor pressure desired. The pressure was determined from the curve of Baxter and Gose.[1] In the case of the furnace tube, a considerable amount of iodine was driven into the experimental tube, and allowed to condense on metal end pieces which were water-cooled. The iodine vapor passing out of the tube during a run acted as a diffusion pump and carried off gaseous impurities from the tube. These end pieces were of large area and were kept at the temperature desired, while the bulb containing the iodine originally was maintained at a higher temperature. In both cases the experimental tube was kept connected to a diffusion pump through two liquid air traps. A short piece of capillary tubing was inserted between the experimental tube and the first trap to prevent too rapid loss of iodine, and to insure the desired pressure. When two liquid air traps were used, no difficulty was experienced in keeping mercury out of the apparatus; whereas when only one trap was employed, mercuric iodide invariably appeared after a time.

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[1] Rays of Positive Electricity.

With the simple tube, the arc struck at or above an average of 14.6 volts and broke at this potential. The pressure was varied from 0.5 to 1.5 mm., the deviation of the critical potential from the average given above being 0.3 volt in the four runs made. With the tungsten furnace, the arc struck at from 10.25 to 36.5 volts depending upon the condition of the tube. As this tube could not be baked out on account of its construction, it was impossible to get entirely free from impurities, although the furnace was run for a considerable time and the tube heated from the inside in this way for two hours before iodine was admitted. The presence of a slight amount of impurity seemed to be sufficient to prevent the striking of the arc at 10.25 volts. On two occasions, once with vapor pressure of 0.3 mm. and the other time at a pressure of 1 mm., the arc was maintained to 10.25 volts. In the former of these runs the arc also struck at this potential. In both cases the filament was as hot as it could be used with safety. In a number of runs the arc struck at about 12 volts, and the average of the breaking potential of 16 runs was 12.1 volts, indicating that this is undoubtedly a critical potential for iodine. Several of the runs showed three sharp discontinuities in the current-potential curve, but there was no agreement in the values of the higher potentials. Iodine probably has several critical potentials, and further investigation to determine them is desirable. It is not surprising that this is the case with so complex an atom as the iodine atom is known to be.

There is no doubt that the iodine was dissociated in the tungsten furnace. Ordinarily the furnace was maintained at a bright yellow heat. Higher temperatures were tried, but there were no differences in the critical points obtained. In fact, the heat of the filament and the action of the arc were sufficient to produce practically complete dissociation inside the furnace cylinder. Calculations based upon the work of Starck and Bodenstein[1] on the thermal dissociation of iodine indicate that the vapor would be completely dissociated at pressures up to 5 mm. at 1200° C.

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[1] Amer. Chem. Soc. Jour., 37, 1016, 1915.

Why it was so difficult to maintain the arc below 12 volts is not clear in as much as the ionizing potential of the iodine atom is usually put at 10 volts or less as is seen from Table III. Compton and Smyth made no attempt to distinguish between radiation and ionization, and, as the total effect in their experiments was small, the ionization produced at the lower potentials may have been due to cumulative action. They point out in their paper that an inspection of Found's published curves shows that there are two break points, a pronounced one at 9.8 volts and another less sharply defined at about 8.3 volts. It would seem, then, that ionization is first definitely detected at about 10 volts, and the 10.25-volt break obtained in this investigation agrees with this within the limits of experimental error. There is no evidence in a comparison of the results of the simple tube and the furnace tube that the molecule is dissociated and one of the atoms ionized at a single impact as there was in the case of hydrogen. While the critical potential obtained from the simple tube is higher than those of the furnace tube, the differences do not correspond to the heat of dissociation of iodine which is equivalent to approximately 1.5 volts. This was a rather surprising result in view of the evidence obtained on this point by Compton and Smyth.

TABLE III.

	Radiating Potential.	Ionizing Potential.
Found[2]	——	8.5
Mohler and Foote[3]	2.34	10.1
Compton and Smyth[4]	——	8.0 atom 9.4 molecule 6.8 fluorescing molecule

Iodine vapor acts quite rapidly on hot tungsten, and the life of a filament or a furnace was short. This made frequent renewals necessary, and so the progress of the investigation was slow and difficult.

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[1] Zeit. Elektrochemie, 16, 966, 1910.

[2] PHYS. REV., 16, 41, 1920.

[3] PHYS. REV., 15, 321, 1920.

[4] PHYS. REV., 16, 501, 1920.

SPECTROSCOPIC OBSERVATIONS ON IODINE.

The line spectrum only appeared in the iodine arc, no trace of any bands being found. With the simple tube a few faint lines appeared, but most of the strong lines were seen with the furnace tube. A few lines flashed in when the arc struck and remained quite strong until the arc broke. The line 4862 was the strongest and most persistent of these and this together with the others of this group have been identified with the "arc" lines listed by Wood.[1] A number of additional lines appeared at higher voltages and increased more rapidly in intensity than those which appeared first. These lines faded out gradually as the voltage was diminished and vanished before the arc broke. They have been identified with other strong lines listed by Wood, being of those which increased in intensity when a spark gap was connected in parallel with his vacuum tube. This manner of appearance suggests that the first lines to appear are due to the neutral atom while the lines coming in later are due to the ionized atom and are enhanced lines. On the basis of the structure of the iodine atom given by the Lewis-Langmuir theory one would expect successive ionizations to occur rather easily.

In conclusion, the writer wishes to express his appreciation to Professor K. T. Compton, under whose direction this work was done, for his many helpful suggestions and unfailing interest during the course of this investigation.

PALMER PHYSICAL LABORATORY,
PRINCETON UNIVERSITY.

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[1] Researches in Physical Optics, Part II.

AN EXPERIMENTAL STUDY OF THE SCATTERING OF APPROXIMATELY HOMOGENEOUS X-RAYS BY POWDERED CRYSTALLINE CARBON, METALLIC LITHIUM, AND LIQUID BENZENE, MESITYLENE, AND OCTANE.

BY C. W. HEWLETT.

SYNOPSIS.

Scattering and Absorption of Homogeneous X-Rays by Carbon (Diamond and Graphite), Metallic Lithium, and the Liquids Benzene, Mesitylene and Octane.— 1. *Scattering curves.* The intensity of the radiation scattered by the substance contained in a small capsule placed at the center of the spectrometer was measured by the ionization method for angles from 2° to 165°. While a ZrO_2 screen was used to isolate the K_α line of Mo (0.712 Å.), some radiation of λ 0.445 Å. was apparently also present. For diamond, graphite and lithium, the maxima agree in position and relative intensity with those found by A. W. Hull by the photographic method. The curves for the liquids, however, are remarkable in that each shows one maximum; 8.5° for benzene, 6.5° for mesitylene and 8.1° for octane, with indications of others unresolved, suggesting that the liquids have a crystal structure. For very small angles the scattering is zero for the solids, and approaches zero for the liquids. 2. *Mass-scattering coefficients* were obtained by integrating the area under the curves, or by experimentally integrating the ionization for all angles of scattering. The coefficients for carbon (diamond and graphite), 0.200, and for lithium, 0.168, agree with Thomson's theoretical values. For benzene, mesitylene, and octane, however, the values 0.238, 0.244, and 0.262 respectively are about ten per cent. larger than those predicted by theory, and give too large specific values for carbon and hydrogen, 0.22 and 0.46 instead of 0.20 and 0.40 respectively. The results are probably accurate to three per cent. 3. *True mass-absorption coefficients*, obtained from the total absorption, the scattering and the density, are found for the solids to be in accord with the theoretical expression $KN^3\lambda^3$, the mean value of K being 4.38×10^{-3}.

Evidence of crystal structure of liquids seems to have been found in the scattering curves for benzene, mesitylene and octane, as suggested above, and the spacings of the planes of atoms responsible for the principal maximum are benzene 4.8 Å., mesitylene 6.3 Å., and octane 5.0 Å.

INTRODUCTION.

THE experiments described in the following report are the outgrowth of a former series of experiments made by the writer[1] in which the mass absorption and mass-scattering coefficients of homogeneous x-rays were studied for several substances as a function of the wavelength of the x-rays. The definitions of these coefficients, and a discussion of the expression $KN^3\lambda^3 + (\sigma/\rho)$ which has been proposed to give the value of the total mass absorption coefficient of x-rays of wave-length λ in an element whose atomic number is N, is given in the paper referred to above. In this former work the total mass-absorption coefficient was measured by determining the intensity of a beam of homogeneous x-rays before and after passing through a screen of the absorbing element. The mass-scattering coefficient deduced from the above equation was found to depart from the theoretical value deduced by J. J. Thomson,[1] and the value of K to depend on the scattering element. Moreover the curves were not found to be linear with λ^3 as they should have been in the region investigated according to theoretical considerations. In particular there seemed to be something anomalous in the behavior of carbon in the neighborhood of wave-length 0.75 Å. which is near the K_α line of molybdenum 0.712 Å. The scattering of hydrogen calculated from the experiments on water and liquid oxygen, and the absorption coefficient of lithium could not be interpreted in the light of theory. It therefore seemed advisable to measure the mass scattering, and the true mass-absorption coefficients for certain elements and wave-lengths independently of one another. The present work, of which a preliminary report[2] was made last November before the American Physical Society, consists of measurements of the scattered x-rays as a function of the angle of scattering from graphite, diamond, lithium, and three liquid compounds of carbon and hydrogen. The radiation falling on the scattering material was the x-radiation from a molybdenum anode tube excited at about 30 kv. The radiation was filtered through a screen of zirconium oxide which absorbed very greatly all the radiation except that in the neighborhood of the K_α line of molybdenum.

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[1] PHYS. REV., N. S., 17, 1921, p. 284.

The general results of the measurements have been expressed in two ways. The intensity of scattering has been plotted as a function of the angle of scattering, and the mass-scattering coefficients and the true mass-absorption coefficients have been tabulated together with other data from which they were directly deduced.

The matter is presented in the following order:

I. Description of Apparatus and Mounting of the Scattering Material.
II. Procedure in the Experiments.
III. Procedure in Calculating the Mass Scattering and the True Mass-Absorption Coefficients.
IV. Sources of Error.
V. Results and Discussion.
VI. Appendix; a Detailed Consideration of a Point arising in III.

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[1] Conduction of Electricity through Gases, 2nd edition, p. 325.

[2] Phys. Rev., N. S., 19, 1922, p. 265.

Description of Apparatus and Mounting of Scattering Material.—The Coolidge tube was mounted on sulphur insulators in a lead-covered wooden box about 2 ft. x 2 ft. x 3 ft. The tube was supplied by a 35 kv. oil-insulated transformer which in turn was supplied by a motor generator set. Regulation of voltage and frequency were obtained by rheostats inserted in the field circuits of the motor generator. A D'Arsonval type milliammeter was inserted in the secondary of the transformer at its midpoint which was grounded. All of the high potential apparatus was enclosed in a wire netting cage and the door into this cage could not be opened without opening the primary circuit of the transformer.

The x-ray spectrometer was constructed in this laboratory, and angular settings could be made with an accuracy within 2′ of arc. The ionization chamber was mounted on wheels so that it could rotate about the axis of the spectrometer. The scattering material was mounted in a small celluloid capsule whose axis coincided with that of the spectrometer. The small table holding the scattering material was caused to rotate continuously about the axis of the spectrometer.

The ionization chamber was 1 foot long. The outside brass cylinder was 4 inches in diameter and was earthed. The inside cylinder was 3¾ inches in diameter, and was kept charged to a potential of about 250 volts by a battery of dry cells. A horizontal electrode insulated by amber was placed in this inner cylinder about half way between its axis and surface. A fine wire was soldered to this electrode and then passed along the axis of a brass tube leading from the ionization chamber to a point in the axis of the spectrometer about 6 inches above the scattering material. From this point the wire passed down the axis of another tube to one pair of quadrants of an electrometer. The movable and fixed tubes were connected by end pieces, one of which could rotate inside the other. The wire joining the electrode to the electrometer was insulated by amber throughout and was completely shielded, all of the shielding being connected together by soldered wires and grounded. The opening in the ionization chamber was 1.50 cm. in diameter, was situated in the horizontal plane passing through the x-ray beam and scattering material and the distance of this opening from the scattering material was 35.5 cm. The electrodes in the ionization chamber were so placed that none of the x-rays from the scattering material could strike them. A lead screen was placed about half way between the scattering material and the opening in the ionization chamber. An opening in this screen was made just large enough to allow every part of the scattering material to send x-rays to every part of the opening. A lead hood was placed over the space between the ionization chamber and this screen to cut off possible radiation from other objects than those in the neighborhood of the axis of the ionization chamber. In order to cut off all unnecessary direct x-radiation there were two lead slits between the box and the scattering material, the one nearest the scattering material being about 10 cm. distant.

The other pair of quadrants of the electrometer were connected to the case of the electrometer and to earth. An earthing key was connected through a resistance of about 1,000 ohms to earth. This resistance was connected to a potentiometer so that the key could be charged to any desired potential or earthed at will. This key dipped into a mercury cup connected to the electrode in the ionization chamber. The electrometer needle was charged to a potential of 100 volts, and the sensitivity ranged from 1,000 to 5,000 divisions per volt in the different parts of the work.

The scattering material was mounted in thin cylinders of circular cross section, which were made by cutting sheet celluloid of 1 mil thickness into strips from $\frac{1}{8}$ to $\frac{3}{8}$ inch in width and wrapping them helically on a brass or steel rod, allowing each turn a narrow lap on the preceding one. This helix was then secured at each end and the helical seam cemented with collodion. These capsules were found to absorb less than one per cent. of the x-rays falling on them. Two sizes of capsules with internal diameters of $\frac{3}{16}$ and $\frac{1}{4}$ inch were used.

The material called artificial graphite was a highly purified carbon which was obtained in compressed cakes. It was finely powdered by filing, and the powder packed into the capsule. The natural graphite was originally in chunks. This material was forced through a sieve of 50 meshes to the inch, and then packed into a capsule. The diamond was in the form of five splints. These splints were very thin and their cross-sectional area ranged from 0.010 to 0.001 sq. cm. The lithium, from a very old exhibition sample, of German manufacture, was squirted through a die into a rod of the required dimensions, and immediately enclosed in one of the celluloid capsules. Fortunately none of the three liquids used in these experiments attacked the capsules.

II. Procedure in the Experiments.

Method of obtaining the data for plotting the curves. The beam of x-rays, which had a rectangular cross section, was adjusted so as to cover the whole width of the capsule of scattering material and to project a short distance on either side. The cross section of the beam in the vicinity of the scattering material was approximately 0.8 cm. square, but this was varied slightly from time to time when different size capsules were used.

The x-ray tube was operated at a potential of about 30 kv. at 60.7 cycles per sec. and the current read on a D'Arsonval type milliammeter was 4 m.a. These conditions of operation were maintained constant to within 1 per cent. throughout the work. A zirconium oxide screen, which reduced the K_α line to about 60 per cent. of its intensity without the screen, and reduced the K_β line to about 6 per cent. of the intensity of K_α line, was placed in the path of the radiation as it emerged from the box containing the tube.

The ionization chamber was set at as small an angle as could be done without allowing any of the direct beam to enter it, the electrometer was charged, the earth connection broken, and the time required for the electrometer deflection to change from one of two definite values to the other was determined. An empty capsule of the same construction as the one containing the scattering material was then substituted for the full capsule, and the time required for the same change in deflection determined. Deducing the rates of deflection, and subtracting that due to the empty from that due to the full capsule, the rate of deflection due to the scattering material was obtained, and this was taken as a measure of the intensity of the scattered radiation entering the ionization chamber. If the intensity was so great that the rate of deflection was no longer an accurate measure of its intensity, the following method was adopted. A lead screen was placed between the scattering material and the ionization chamber, the electrometer charged, the earth connection broken, and the deflection noted. The lead screen was then removed for a definite interval of time and then replaced. When the deflection became constant its value was again noted. Whenever necessary, account was taken of the rate of deflection with the lead screen in place. In this way the intensity was determined from point to point, the steps in most cases being less than the angle subtended by the opening in the ionization chamber at the scattering material, particularly in the region of a pronounced maximum. When once the position of the principal maximum of scattering was known, measurements were made frequently at this setting, to check the constancy of operation. Finally the intensity at the various angles was expressed as percentages of the intensity at the principal maximum.

In order to calculate from the scattering curve the fraction of the incident energy which was scattered it was necessary to know the ratio between the flux of radiation into the ionization chamber at some particular setting and the flux of energy falling on the scattering material; and in addition, the total mass-absorption coefficient of the radiation in the scattering material. These quantities were usually determined at the beginning and at the end of each series of measurements of the intensity. Two methods were used in determining the above ratio and the total mass absorption coefficient.

In the first method a thin lead sheet through which had been bored a circular hole about 0.10 cm. in diameter was placed immediately behind the capsule so that the beam of x-rays through the hole passed through the axis of the capsule. A lead disc mounted on the axle of a small electric motor was placed between the capsule and the ionization chamber with its face perpendicular to the beam of x-rays. The axis of the ionization chamber was set to coincide with that of the beam of x-rays. There was a narrow radial slit in the disc so that when the disc was in rotation the small beam passing through the circular hole entered the ionization chamber for a short interval once during each revolution of the disc. By this means it was found possible to secure a conveniently measurable fraction of the energy flux falling on the capsule. This fraction of the energy flux was calculated from the cross section of the x-ray beam striking the capsule when unobstructed by the lead sheet, the area of the hole, and the angular width of the slit in the lead disc. The cross section of the x-ray beam falling on the capsule was deduced from an x-ray shadow picture made by the x-ray beam on a photographic film placed perpendicular to the x-ray beam and in contact with the full capsule, the beam passing first through the capsule, then striking the film. The width of the shadow of the capsule checked with the diameter of the capsule. The diameter of the hole was measured with a micrometer microscope. The total mass-absorption coefficient of the radiation in the scattering material was determined from measurements of the energy flux through the small hole and rotating disc, determined alternately when the x-rays passed through the full and the empty capsule.

There are two objections to the method outlined above; namely, a flash of x-rays entering the ionization chamber is not representative of the average intensity of the beam, but is a very small section of the radiation emitted during one cycle of the alternating current. The number of these flashes received by the chamber during a determination is very large, however, and unless the disc should have a speed bearing a simple relation to the frequency of the alternating current from the transformer, this consideration should not lead to undesirable results. On the other hand, the thin lead screen with the small hole had to be adjusted very accurately perpendicular to the x-ray beam, for it had a thickness comparable with the diameter of the hole. This consideration led to the adoption of another method for determining the total mass-absorption coefficient and the ratio of the energy flux falling on the capsule to that entering the ionization chamber at a definite setting.

The following method was designed to allow the total energy flux falling on the capsule to pass into the ionization chamber for the time of one complete cycle of the alternating current from the transformer. A lead disc carrying an angular slit of adjustable width was mounted on a horizontal axle, so that in rotating, the beam of x-rays was allowed to pass through the slit when the latter was vertical. This disc and axle was controlled by a stiff steel helical spring in the same manner as the balance wheel of a watch. Two stops with trigger action were arranged so that one of them could hold the disc displaced from its vertical position by a definite amount, and upon release, the other stop would catch and hold the disc at the end of its first swing. By successive adjustments of the stiffness of the spring, the width of the slit, and the height of the stops, the time for the slit to sweep across a point in the x-ray beam was made equal to the period of the alternating current to within 1 per cent. In order to determine when the adjustment was completed, the face of the disc was covered with a thin film of smoke and a vibrating reed operated by the alternating current supplying the transformer traced a curve on the disc as it swung. The disc was mounted close to the box containing the tube, where the cross section of the beam was a minimum. Obviously it makes no difference what part of the cycle the exposure begins if it lasts one complete cycle.

A lead slit open at the lower end and having a width equal to that of the capsule was placed on the capsule when making measurements of the direct beam, so that only the portion of the beam striking the capsule could pass on to the ionization chamber. The opening in the ionization chamber was large enough to receive all of the radiation which passed through the capsule, and the exact position of the chamber was secured with the aid of a fluorescent screen.

The procedure was as follows: with the empty capsule in place the lead disc was secured by one of the stops. The electrometer was charged, the earth connection broken, and the electrometer deflection noted. The stop was tripped, allowing the disc to swing. The deflection of the electrometer changed rapidly, and became constant again in about one minute, at which time its value was again noted. From the change in deflection the charge given to the insulated system was computed, and this was taken as a measure of the radiation falling on the capsule during one cycle. The full capsule was then substituted for the empty one, and the procedure repeated, from which was computed the radiation transmitted through the scattering material during one cycle. A number of such determinations were made at each experiment, those with the empty and full capsules being distributed in such a manner that the mean values of each corresponded to the same epoch. The intensity of the scattered radiation for the principal maximum of the scattering material was next determined in the manner already described.

By multiplying the ordinates of a scattering curve by the sine of the angle of scattering, and by a factor to take account of the size of the angular opening of the ionization chamber measured from the scattering material, a new curve was obtained, the area under which gave the total amount of scattered radiation in terms of the radiation falling on the scattering material. This procedure rests upon the assumption that an element of the scattering material containing a large number of small crystals would scatter radiation equally in all directions making a given angle with the direction of the direct beam.

The following method was devised so that the procedure of calculation from the scattering curve just described would be done automatically by the method of measuring the scattering. Having first measured the intensity of the direct beam through the empty and full capsules, the ionization chamber was set close to the direct beam. With a lead screen in front of the chamber the electrometer was charged, the earth connection broken, and the deflection noted. At a definite instant, which was recorded beforehand, the lead screen was removed and the ionization chamber moved along from degree to degree, leaving it on each degree for an interval of time proportional to sin θ, where θ was the angular setting of the chamber from the direct beam. The schedule for moving the chamber was prepared beforehand, and was so designed that the amount of radiation entering the ionization chamber during its tour around the circle was equal to the total amount of radiation scattered in 1 second.

The total charge taken by the electrometer during its tour around the circle was then proportional to the total x-rays scattered during 1 second. This total charge was deduced from the total change in deflection of the electrometer. This procedure was carried through for the empty capsule and for the full capsule in such a manner that the results for each corresponded to the same epoch. At the end, the intensity of the direct beam was again measured through the empty and full capsules.

III. Procedure in Calculating the Mass-Scattering Coefficient and the True Mass-Absorption Coefficient.

1. Calculation of the total mass-absorption coefficient $(\mu + \sigma)/\rho$. The densities of the materials in the capsules were determined, in the case of the solids, by dividing the mass of the material packed in the capsule by the volume of the capsule; in the case of the liquids by finding the loss in weight of a sinker of known volume when suspended in them.

When the small hole and rotating disc were used for measuring the total mass-absorption coefficient, this quantity was given by the expression

$$d = \epsilon^{-\frac{\mu+\sigma}{\rho}\cdot t},$$

where t is the average length of path of the x-rays through the scattering material, and d is the ratio of the intensity of the beam through the full capsule to that through the empty capsule.

When one cycle of the x-rays falling on the capsule was allowed to enter the ionization chamber the total mass-absorption coefficient was calculated from the following expression:

$$d = 1 - \frac{\pi}{4}b + \frac{1}{3}b^2 - \frac{\pi}{32}b^3 + \frac{1}{45}b^4 - \cdots,$$

where

$$b = \frac{\mu + \sigma}{\rho}D.$$

D is the diameter of the capsule.

2. Calculation of the fraction of the x-rays falling on the scattering material that was scattered. When using the scattering curves the first procedure was to multiply the ordinates of the scattering curve by the factor

$$\frac{2 \sin \delta}{1 - \cos \delta} \sin \theta,$$

where δ is half the plane angle subtended at the scattering material by the opening in the ionization chamber, and θ is the angle from the direct beam at which the scattering was measured. The area under this new curve was then found, using 2δ as the unit abscissa and 100 per cent. as the unit ordinate. This area is equal to the total measured scattered x-rays in terms of that measured at the angle of maximum scattering. The number for the total measured x-rays was then corrected by estimation for the scattering between 165° and 180° inaccessible to the ionization chamber. This correction usually amounted to 1 or 2 per cent. of the total measured x-rays. Next the correction for absorption in the scattering material (see appendix) was applied, giving the total scattered x-rays in terms of that measured at the angle of maximum scattering. Finally, this number was divided by the ratio of the energy flux falling on the scattering material to that entering the ionization chamber at the angle of maximum scattering, giving the fraction of incident x-rays that was scattered.

When the scattering was measured by rotating the ionization chamber from degree to degree the total measured scattered x-rays for the empty capsule were subtracted from that for the full capsule, and the corrections for the region inaccessible to the ionization chamber and for the absorption in the scattering material were applied. This gave the total x-rays scattered in 1 second which was then divided by the x-rays falling on the scattering material in 1 second.

3. Calculation of the mass-scattering and the true mass-absorption coefficients. When one cycle of the radiation falling on the capsule was allowed to enter the ionization chamber, the amount of the direct beam taken out by the scattering material is given directly by $1 - d$. When the small hole and rotating disc was used the fraction of the direct beam of x-rays taken out by the scattering material was calculated from the expression

$$\frac{\pi}{4}b - \frac{1}{3}b^2 + \frac{\pi}{32}b^3 - \frac{1}{45}b^4 + \cdots,$$

where

$$b = \frac{\mu + \sigma}{\rho}D.$$

Let this fraction be denoted by T, while S denotes the fraction of the incident beam scattered. Then since scattering and absorption take place together

$$\frac{S}{T} = \frac{\sigma}{\mu + \sigma},$$

so that the mass-scattering coefficient is given by

$$\frac{\sigma}{\rho} = \frac{S}{T} \cdot \frac{\mu + \sigma}{\rho}.$$

Each of the three quantities on the right were measured so that σ/ρ could be calculated. The true mass-absorption coefficient was then obtained by subtracting the mass-scattering coefficient from the total mass-absorption coefficient.

IV. Sources of Error.

1. On account of the finite size of the scattering material there is some indefiniteness as to its centroid. The volume of the scattering material was about 0.10 cm.^{3} and 0.20 cm.^{3} for the smaller and larger capsules respectively.

2. The x-rays were not parallel at the scattering material, so that the total mass-absorption coefficients as calculated would be slightly in error. The distance from the source of x-rays to the scattering material was 1 meter.

3. Saturation voltage in the ionization chamber was secured by trial, and then twice that voltage allowed as a factor of safety.

4. The electrometer scale was not absolutely uniform, but the proper corrections were applied wherever necessary.

5. The variation of voltage, frequency, and thermionic current through the tube would introduce serious errors in work of this kind if not carefully controlled. All of these were carefully regulated by hand, frequently one person giving this his entire attention.

6. Variation in the effective amount of methyl bromide in the ionization chamber during a series of experiments. Although this was at times rather large, standardizing measurements were made at the beginning and end of each series, and frequently during the series, so that it was possible to allow by interpolation for uniform changes such as the above.

7. Non-uniformity of the density of the scattering material in the capsules. In the case of the liquids this consideration does not enter, and in the case of the diamond splints it is safe to conclude that the effect is negligible. With the two kinds of graphite every precaution was taken to insure uniformity of distribution by careful packing, and the observations were made allowing the x-rays to fall on different sections of the capsule. In the case of the lithium there is a possibility (hardly probable) of blow holes. These blow holes might even be filled with some of the oil in which the lithium had been kept.

8. The adjustment of the small hole behind the scattering material in the one method for measuring the absorption coefficient and the adjustment of the slit on the scattering material in the other method were made with great care as a small displacement of these limiting devices would lead to a relatively large error in the results.

All of these main sources of error and several other minor ones have been carefully considered and it is estimated that the final results are not in error by more than 3 per cent. on account of them.

V. Results and Discussion.

Table I. gives the results on the mass-scattering and the true mass-absorption coefficients of the substances given in the first column. The second column gives the method used in the determination, the number in brackets showing the number of separate determinations from which the values in a given line were deduced.

Method *A* signifies that the calculations were made from the scattering curve for the material. The comparison with the direct beam of x-rays in these calculations was determined by allowing one cycle of the x-rays falling on the capsule to enter the ionization chamber. In method *B* the ionization chamber was moved from degree to degree allowing the charge on the electrometer to accumulate. The comparison with the direct beam of x-rays in these calculations was determined by the small hole and rotating disc method. Method *C* differed from method *B* in that the comparison with the direct beam was as in method *A*. The third column gives the percentage *S*, of the x-rays falling on the scattering material, which was scattered. The fourth column gives the fraction *F*, of the x-rays falling on the scattering material, which was removed by the combined processes of absorption and scattering. The fifth, sixth, and seventh columns give the total mass-absorption coefficient, the mass-scattering coefficient, and the true mass-absorption coefficient respectively. The eighth column gives the means of the mass-scattering coefficient for each substance. The ninth column gives the value of *K* calculated from the expression $\mu/\rho = KN^3\lambda^3$ where μ/ρ is the true mass-absorption coefficient.

A comparison of the position of the maxima in the scattering curves for the solid substances shows good agreement with those obtained by Hull[1] using the photographic method. The relative intensities of the various maxima agree as well as might be expected considering the degree of uncertainty that lies in estimating relative intensities from blackening of photographic plates.

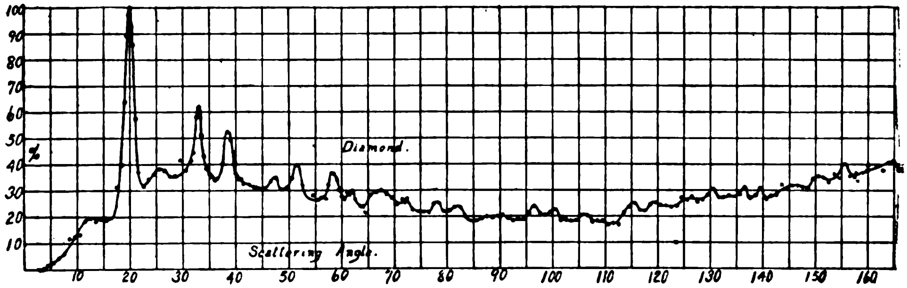

Fig. 1.

A novel point of interest shown by the curves and previously reported by the writer[2] is that for the solid substances the scattering becomes zero for very small angles from the direct beam, and approaches zero for the liquids. A special experiment was carried out to check this fact. A lead slit about 3 mm. wide was placed over the opening in the ionization chamber and it was found that at 2° from the direct beam the liquids

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[1] Phys. Rev., N. S., 10, 1917, p. 661.

[2] Phys. Rev., N. S., 17, 1921, p. 284.

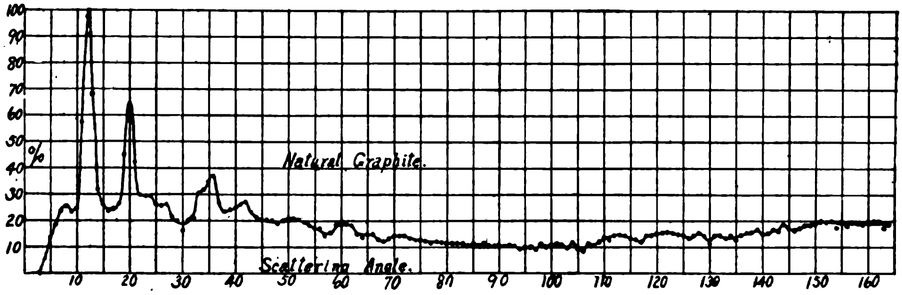

Fig. 2.

scattered less than 10 per cent. as much as at the angle of maximum scattering, while for graphite and diamond the scattering was zero at angles of 5° and 6° respectively. Since this fact was published, A. H. Compton[1] has given a theoretical discussion in which he has shown that the scattering would be expected to become zero for small angles in the case of crystalline material. A quantitative explanation of this behavior for the liquids is as yet not forthcoming. It will be noticed that there is a prominent maximum which occurs for the solid substances at a smaller

TABLE I.

1.	2.	3.	4.	5.	6.	7.	8.	9.
Substance.	**Method.**	S%.	F%.	$\frac{\mu+\sigma}{\rho}$.	$\frac{\sigma}{\rho}$.	$\frac{\mu}{\rho}$.	Mean $\frac{\sigma}{\rho}$.	K.
Diamond Splints......	$A(1)$	11.86	26.1	.428	.195	.233	.199	4.40×10^{-8}
Diamond Splints......	$B(10)$	12.16	31.7	.515	.198	.317		4.44
Diamond Splints......	$C(2)$	12.19	29.6	.497	.205	.292		4.33
Natural Graphite.....	$A(1)$	6.55	18.6	.553	.195	.358	.201	4.53
Artificial Graphite....	$A(1)$	6.33	17.4	.551	.200	.351		4.33
Artificial Graphite....	$B(7)$	6.49	17.4	.551	.206	.345		4.26
Artificial Graphite....	$C(3)$	6.35	15.2	.477	.199	.278		4.35
Metallic Lithium.....	$A(1)$	4.21	5.78	.217	.158	.059	.168	4.36
Metallic Lithium.....	$C(4)$	4.14	4.80	.206	.178	.028		
Benzene............	$A(1)$	9.28	18.6	.478	.238	.240	.238	
Benzene............	$B(3)$	6.90	14.7	.497	.233	.264		
Benzene............	$C(3)$	6.69	13.8	.468	.227	.240		
Benzene............	$C(1)$	9.70	21.6	.567	.255	.312		
Mesitylene..........	$A(1)$	9.39	18.4	.478	.244	.234	.244	
Mesitylene..........	$B(2)$	6.83	14.4	.489	.232	.257		
Mesitylene..........	$C(2)$	7.02	12.8	.431	.236	.195		
Mesitylene..........	$C(1)$	9.89	21.3	.564	.262	.302		
Octane..............	$A(1)$	8.05	15.5	.496	.258	.238	.262	
Octane..............	$C(1)$	8.29	16.3	.524	.266	.258		

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[1] Not yet published.

angle than the principal maximum which corresponds to a wave-length 0.712 Å. Assuming that this maximum at the smaller angle is due to

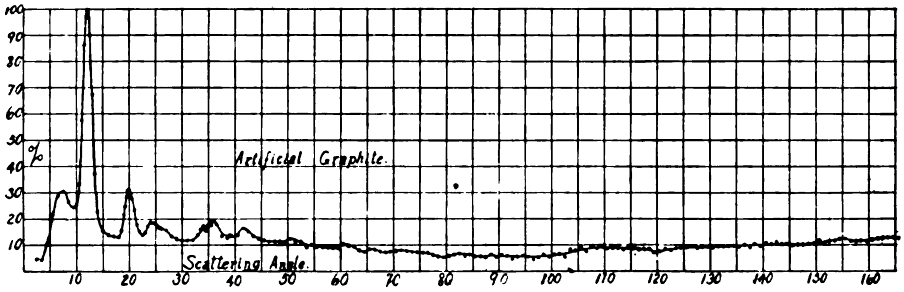

Fig. 3.

the short wave-length radiation which gets through the Zr filter, the effective wave-length was calculated from the data on diamond graphite and lithium supposing that this maximum was due to reflection from the set of planes giving the principal maximum in each case. This gave the effective wave-length of this radiation as 0.446, 0.441, and 0.449 Å.,

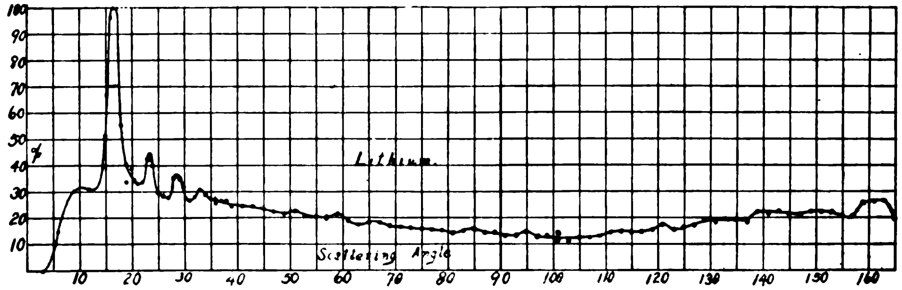

Fig. 4.

for the three substances in the order named. The mean value for this wave-length is then 0.445 Å. This explains the appearance of the maximum occurring in the neighborhood of 25° in the curve for diamond, for this is the correct position for second-order reflection of wave-length 0.445 Å. from the 111 planes.

The appearance of a very pronounced maximum at a small angle for each of the liquids investigated points very strongly toward the view that these liquids have something of a crystal structure. These maxima occur at rather small angles, and consequently the maxima due to the first two or three orders of reflection for the wave-length 0.445 Å. would overlap the first two due to the wave-length 0.712 Å. It will be seen that this idea readily lends itself to explain the relatively complicated structure of the maxima, and the slightly irregular course of the scattering curves for the liquids between 10° and 25° scattering angle. The capsules containing the liquids from which these curves were obtained were 0.25 inch in diameter, so that the overlapping would be greater than with the smaller capsules (0.187 inch in diameter) which were used for graphite and diamond. The scattering curves for these liquids for the first 25° have been studied very carefully, using capsules 0.187 inch in diameter, and a slit 3 mm. wide across the opening in the ionization chamber. With this arrangement the complicated structure of the maxima shown in the curves in this paper have been resolved into separate maxima, and the position of the principal maximum due to wave-length 0.712 Å. found as follows: benzene 8°.5, mesitylene 6°.5, octane 8°.1. The distances between the planes of atoms responsible for these maxima are as follows: benzene 4.8 Å., mesitylene 6.3 Å., octane 5.0 Å.

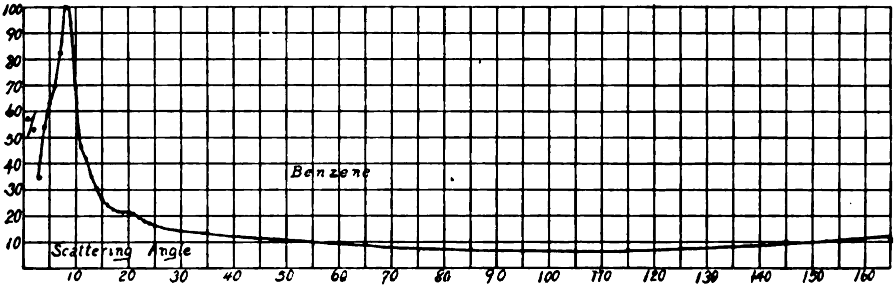

Fig. 5.

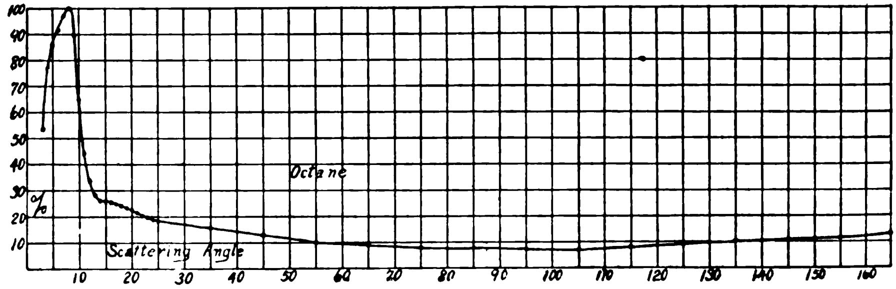

Fig. 6.

Very little information can be drawn from the curves in regard to the intensity of reflection from the crystal planes in the successive orders, for the number of sets of planes coöperating at a given angle of scattering in the case of powdered crystals is too great. Since there are an infinite number of sets of planes in any given crystal lattice, the number of coöperating sets at any given angle of scattering would be very great, and would be greater the smaller the individual crystals of the material. This point is illustrated by a comparison of the curves for natural and artificial graphite. The artificial graphite was more finely powdered than the natural graphite, and the maxima for the latter stand out more prominently than for the former. The curves indicate, however, that the reflections in the successive orders decrease at least as rapidly as the inverse square of the order of reflection.

It should be mentioned that the shape of the scattering curves depends to some extent on the dimensions of the scattering material and the opening in the ionization chamber; the changes in the curves becoming more abrupt the smaller these dimensions. The relative heights of the maxima and minima would also be slightly dependent on these considerations. The radiation falling on the scattering material contains, besides the K_α line of molybdenum, an appreciable amount of shorter wave-length radiation, which fact in itself complicates the interpretation of the curves to a certain extent. With different thicknesses of filtering material the scattering curves would be different. The more homogeneous the radiation the more prominent, and the sharper would be the maxima of the curves. But even with constant filter thickness, dimensions of apparatus, and conditions of tube operation, there is still a factor which affects the experimental scattering curves. The ionization chamber is not long enough to absorb all the radiation which enters it; especially is this true for the short wave-length radiation. When the ionization chamber had been freshly filled with methyl-bromide gas the short wave-length radiation was absorbed to a much greater extent by the gas than a few days later when the gas had become less susceptible to ionization. The longer wave-length radiation of the K_α line was

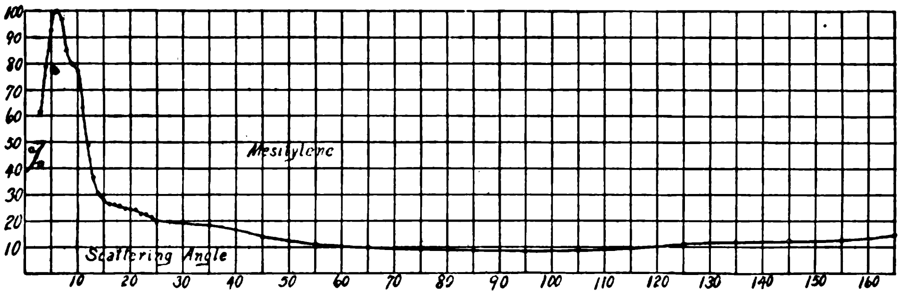

Fig. 7.

absorbed almost to the same extent when the chamber was freshly filled, and for a few days thereafter. It may readily be seen that the experimental scattering curve, with a given distribution of radiation falling on the scattering material, will depend upon the density of methyl-bromide gas in the ionization chamber; the maxima will be sharper and more pronounced, the less the density of the gas. For the sake of uniformity and in order to have large ionization currents which could be measured with accuracy, the curves shown in this paper were determined in the interval between freshly filling the ionization chamber and a time when the ionization current had fallen to half value with a constant intensity of x-rays. In the other part of the work where the ionization chamber was rotated continuously so as to automatically integrate the scattered radiation, the density of the gas in the ionization chamber varied widely. It is noticeable in this connection that although the total and true mass-absorption coefficients varied through a wide range for a given substance the mass-scattering coefficient was nearly constant. This is to be explained by the variation in the amount of methyl-bromide gas in the ionization chamber. Since there is both short and long wave-length radiation present the ionization chamber will give a relatively greater importance to the short wave-length radiation when freshly filled than some time later, so that the effective wave-length for ionization will be shorter the greater the density of methyl bromide in the chamber. According to theoretical considerations the mass-scattering coefficient is independent of the wave-length (over certain regions of wave-length this is not true) while the true mass-absorption coefficient in this region of wave-length should be proportional to the cube of the wave-length.

In order to test the above proportionality, the factor of proportionality was calculated for diamond, graphite, and lithium from the equation $\mu/\rho = KN^3\lambda^3$. The value of λ to be substituted in this equation was determined for diamond and graphite by reading off from the absorption curve for carbon previously published by the writer the wave-length corresponding to the value for the total mass-absorption coefficient. The value of the wave-length for lithium was taken to be the same as that for natural graphite as the conditions of operation were about the same in the two cases. It is noticeable that K is nearly the same for diamond, graphite, and lithium, its mean value being 4.38×10^{-3}. This contradicts the writer's former work on lithium where K and the absorption coefficient were found to be abnormally high. The lithium used in the former experiments must have been impure. At least it is known that potassium chloride was mixed with the lithium chloride in the electrolytic separation of the lithium.

From the data given in the table it is seen that the mass-scattering coefficient for carbon agrees with the theoretical value calculated by J. J. Thomson,[1] the average values for graphite and for diamond agreeing with one another and with the theoretical value, 0.200, within the limit of experimental error. The mass-scattering coefficient is thus seen to be independent of the crystal structure. The mean value for lithium 0.168 comes within 3.5 per cent. of the theoretical value 0.174. The mass-scattering coefficients found for the liquids varied somewhat erratically, moreover they are greater than the theoretical values assuming the mass-scattering coefficient of carbon and hydrogen to be 0.200 and 0.399 respectively. The theoretical values for benzene, mesitylene, and octane are 0.215, 0.220, and 0.231 respectively, while the means of the experimental values are 0.238, 0.244, and 0.248 respectively. Assuming that these experimental mass-scattering coefficients are each made up of two parts, one due to carbon and one due to hydrogen, each part in proportion to the mass of carbon and hydrogen present respectively, the mass-scattering coefficients of carbon and hydrogen were calculated to be 0.228 and 0.375 respectively. The value thus found for hydrogen comes within 6 per cent. of the theoretical value 0.399, while the value for carbon is 14 per cent. higher than the value found for graphite and diamond. The mass-scattering coefficients of the three liquids found by method *A* furnish probably a more just basis for determining the separate coefficients for carbon and hydrogen than the above calculation, for the three curves were determined simultaneously point for point. The three equations for the three substances are:

For benzene $12C + H = 3.100,$
For mesitylene $9C + H = 2.440,$
For octane $16C + 3H = 4.893,$

where C and H represent the mass-scattering coefficients of carbon and hydrogen respectively. These equations give three independent values for C and H.

	C.	H.
	0.220	0.488
	0.221	0.441
	0.220	0.460
Means,	0.220	0.463

It is seen that both the values of C and H are considerably larger than the theoretical values. If these liquids contained very small percentages of some element of moderately large atomic weight, such as bromine, some of the absorbed x-rays reëmitted as characteristic x-radiation would be of sufficient penetrating power to reach the ionization chamber where it would add to the effect of the scattered radiation. At least this hypothesis is plausible in the case of the octane, for bromine was one of the constituents of one of the compounds from which it was prepared. The origin of the benzene and mesitylene is not known, but their boiling points and densities indicate that they are relatively pure. One might look for some such effect as proposed above by the method devised by A. H. Compton.[2] This was tried at the angle of maximum scattering for benzene with a negative result.

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[1] Conduction of Electricity through Gases, 2nd edition, p. 325.

VI. APPENDIX. CORRECTION FOR ABSORPTION OF THE SCATTERED RADIATION WITHIN THE SCATTERING MATERIAL.

Attempts to arrive at a complete solution of this problem have not succeeded.

Making the usual assumption of exponential absorption of the x-rays, let $(\mu + \sigma)$ be the linear absorption coefficient, where μ represents that part of the coefficient due to true absorption, and σ that due to scattering. Let us suppose that the distance of the source of x-rays from the scattering material is great enough so that the x-rays are parallel in passing through. This condition is sufficiently fulfilled in the present work. It may then be shown that of a beam of x-rays striking a circular cylinder of material perpendicular to its axis, a fraction is scattered per unit solid angle in the direction making an angle θ with the beam, given by the following expression:

$$S_\theta = f(\theta)\left(1 - \frac{4}{3\pi}a + \frac{1}{8}a^2 - \frac{4}{45\pi}a^3 + \frac{1}{192}a^4 - \cdots\right),$$

where $a = (\mu + \sigma)D$ and D is the diameter of the cylinder $f(\theta)$ is a factor depending on the crystal structure, expressing the angular distribution of the scattered radiation. Not all of this scattered radiation gets out of the scattering material because it is absorbed and scattered on its way out. If it assumed that none of S_θ which is rescattered gets out, we arrive at the following expression for the fraction of the original beam getting out of the cylinder per unit solid angle in the direction making an angle θ with the beam

$$S_\theta' = f(\theta)\int_{-R}^{+R}\int_{-\sqrt{R^2+x^2}}^{+\sqrt{R^2-x^2}} \epsilon^{-(\mu+\sigma)[x+\sqrt{R^2-y^2}+\sqrt{R^2-(x\sin\theta+y\cos\theta)^2}-x\cos\theta+y\sin\theta]}\,dxdy,$$

where R is the radius of the cylinder. The origin of coördinates is taken on the axis of the cylinder. The above assumption is not justifiable, and consequently S_θ' given above is too small. The first four terms of the expansion in powers of a, of the above integral, which were found for me by Prof. E. W. Chittenden, of the department of mathematics at this university, are as follows:

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[2] PHYS. REV., N. S., 18, 1921, p. 96.

$$S_\theta' = f(\theta)\left[1 - \frac{8}{3\pi}a + \frac{1}{4}\left(1 - \frac{\cos\theta}{4} + \frac{\gamma(\pi-\gamma)}{2\pi\sin\gamma} + \frac{\pi-2\gamma}{4\pi}\cos\gamma + \frac{\sin\gamma}{\pi}\right)a^2 \right.$$
$$\left. - \frac{24}{45\pi}\left(1 - \frac{7}{22}\cos\theta + \frac{1}{22}\cos^2\theta - \frac{1}{22}\cos^3\theta + \frac{1}{22}\cos^4\theta\right)a^3\right],$$

$$a = (\mu + \sigma)D$$

and

$$\gamma = \theta \quad \text{if} \quad 0 \leqq \theta \leqq \frac{\pi}{2},$$
$$\gamma = -\theta \quad \text{if} \quad -\frac{\pi}{2} \leqq \theta \leqq 0,$$
$$\gamma = \pi - \theta \quad \text{if} \quad \frac{\pi}{2} < \theta \leqq \pi,$$
$$\pi = \pi + \theta \quad \text{if} \quad -\pi \leqq \theta < -\frac{\pi}{2}.$$

The ratio S_θ/S_θ' gives the correction factor for a given angle θ, that is the number by which the measured scattered radiation must be multiplied to give the actual amount scattered. This factor will be too large, however, because, as mentioned above, S_θ' is too small. The diamond splints being the substance requiring the largest correction factor, calculations were made for it for nine values of θ from 0 to π. The factor has its largest value 1.228 at 0 and continuously decreases to its smallest value 1.200 at π, the value 1.216 at $\pi/2$ being almost the mean of the other two.

Now we may get another estimate of the correction factor by assuming that all of the originally scattered radiation which is rescattered gets out. With this assumption the fraction of the original beam getting out of the cylinder per unit solid angle in the direction making an angle θ with the beam is given by the following expression:

$$S_\theta'' = f(\theta)$$
$$\times \int_{-R}^{+R}\int_{-\sqrt{R^2-x^2}}^{+\sqrt{R^2-x^2}} \epsilon^{-\mu[x+\sqrt{R^2-y^2}+\sqrt{R^2-(x\sin\theta+y\cos\theta)^2}-x\cos\theta+y\sin\theta]-\sigma\sqrt{(R^2-y^2}+x)}\,dx\,dy.$$

Since the previous integral when solved varied so little with the angle θ it was deemed sufficient to solve the above expression for $\theta = 0$. Now this expression will give too large a value for the scattered radiation getting out of the cylinder, and too small a value for the correction factor for some of the rescattered radiation will be absorbed. The above integral when solved for $\theta = 0$ gives

$$S_\theta'' = f(\theta)\left(1 - \frac{4}{3\pi}\frac{b^2 - a^2}{b - a} + \frac{1}{8}\frac{b^3 - a^3}{b - a} - \frac{4}{45\pi}\frac{b^4 - a^4}{b - a} + \cdots\right),$$

where $a = \mu D$; $b = (\mu + \sigma)D$.

The values of S_θ/S_θ' and S_θ/S_θ'' for $\theta = 0$ for the diamond capsule were respectively 1.228 and 1.130. The mean value of this is 1.179, and since the value 1.228 for $\theta = 0$ was about 1 per cent. larger than the mean value, the value 1.17 was taken as the average correction factor for the diamond capsule. In the case of the other materials the difference between the two estimates of the correction factor were much smaller. For instance for the artificial graphite the two values were 1.11 and 1.07, giving a mean value of 1.09.

The writer takes pleasure in recording the following acknowledgments: To Tiffany and Co. of New York City for lending the diamond splints; to Prof. L. C. Raiford for the mesitylene; to Mr. John R. Couture for the benzene and octane; to Prof. P. A. Bond for the lithium; to Dr. A. W. Hull for the graphite and zirconium-oxide filter used in this investigation; to Mr. J. B. Dempster for much help in the construction and design of the apparatus; to Miss Marcella Lindeman, Mr. Joseph L. Fiala, Mr. Harlan Porter and other students in this laboratory for help in taking observations.

STATE UNIVERSITY OF IOWA,
IOWA CITY, IOWA,
June 9, 1922.

ABSORPTION COEFFICIENTS FOR HOMOGENEOUS X-RAYS.

By E. G. Taylor.

Synopsis.

Absorption Coefficients of Various Organic Liquids for X-rays of Wave-length 0.715 Å.—By means of a spectrometer with narrow lead slits and a calcite crystal, the K_α radiation from the Mo target of a Coolidge tube was reflected into an ionization chamber, and the effect of interposing a cell containing a known thickness of liquid before the first slit, was measured. Thus absorption coefficients were determined for carefully purified samples of *pinene* ($C_{10}H_{16}$), *limonene* ($C_{10}H_{16}$), *benzene* (C_6H_6), *toluol* (C_7H_8), *isopropyl alcohol* (C_3H_8O), *methyl proprionate* ($C_4H_8O_2$), *ethyl acetate* ($C_4H_8O_2$), *acetone* (C_3H_6O), *ethyl formate* ($C_3H_6O_2$) and *trimethylene glycol* ($C_3H_8O_2$).

Atomic absorption coefficients for C, H, and O for X-rays of wave-length 0.715 Å. were computed from the above data, assuming absorption to be an additive atomic property, and came out from 11.00 to 11.55×10^{-24} for C, 0.45 to 0.50×10^{-24} for H and 29.9 to 31.0×10^{-24} for o. Using the mean values, the computed coefficients are within $\frac{1}{2}$ per cent. of the observations, on the average. But the fact that the computed values for acetone and water are 1 per cent. too low suggests that the *assumption that absorption is an atomic property* may not be accurately true.

THIS research was undertaken to obtain new data upon the absorption of x-rays because of the great variation in the results obtained by different investigators. The work of Hull,[1] Richtmyer and Grant,[2] Richtmyer,[3, 4] Hewlett[5] and Bragg[6] has shown that for homogeneous x-rays the absorption is proportional to the cube of the wave-lengths of the incident radiation. This emphasizes the desirability of working with as near pure monochromatic radiation as possible.

In this work the author proceeded first to determine the molecular absorption of several organic compounds. If one assumes an additive relation for molecular absorption it is then possible to determine the atomic absorptions of the constituent elements. In this way the atomic absorption coefficients were determined for hydrogen, carbon and oxygen for the wave-length 0.715 Å.

[1] Phys. Rev., Vol. 8, p. 326, 1916.

[2] Phys. Rev., Vol. 15, p. 547, 1920.

[3] Phys. Rev., Vol. 17, p. 264, 1921.

[4] Phys. Rev., Vol. 18, p. 13, 1921.

[5] Phys. Rev., Vol. 17, p. 284, 1921.

[6] Phys. Mag., Vol. 28, p. 626, 1914.

The molecular absorption is defined as that fraction of the incident radiation which is absorbed per molecule per square centimeter of surface normal to the direction of the pencil of rays. In this work the absorption means the total decrease of the incident radiation which includes the "true absorption" and the scattering effect. The molecular absorption was computed from the mass absorption through the relation,

$$M = \frac{\mu}{\rho} m,$$

where M represents the absorption of the molecule,
m represents the actual mass of the molecule,
μ represents the absorption of substance as determined,
ρ represents the density of substance used.

In this computation the mass of the hydrogen atom has been taken as 1.64×10^{-24} gms.

The hydrocarbons used for the determination of the atomic absorptions of hydrogen and carbon were pinene, limonene, benzene and toluol. The atomic absorptions were then determined from two simultaneous equations involving the molecular absorptions of two different compounds. For example the following equations:

$$\begin{aligned} 10\mu_c + 16\mu_H &= 1.209 \times 10^{-22}, \\ 6\mu_c + 6\mu_H &= 0.707 \times 10^{-22}. \end{aligned}$$

Apply to pinene and benzene respectively, μ_c and μ_H representing the atomic absorptions of carbon and hydrogen and the right members representing the molecular absorptions of the compounds.

Having determined the atomic absorptions of hydrogen and carbon the absorption of the oxygen atom was determined from the molecular absorptions of several organic compounds containing oxygen.

METHOD.

The general method of making these measurements did not involve any essentially new principle. The radiation used was that of the K_a line from a molybdenum-target Coolidge tube. The radiation first passed through two very narrow lead slits which limited the divergence of the beam to a few minutes of angle. The emergent radiation was then incident upon a calcite crystal set at the proper angle to reflect the K_a line in the first order. After reflection the radiation passed through another slit into the ionization chamber.

The central electrode of the ionization chamber was supported in a bakelite insulator and connected to the leaf of a Bumstead electroscope.

Methyl iodide or ethyl bromide was used to increase the ionization. Considerable difficulty was experienced with leakage when the vapor density approached that of saturation. By using an ionization chamber approximately 70 cms. long sufficient ionization was produced when the vapor density was low in which case the leak became negligible or could easily be corrected for. The intensity of radiation was measured by the rate of change of potential of the central electrode as indicated by the electroscope.

The various solutions were held in a small bakelite cell while the absorption determinations were being made. This cell was placed in front of the first slit and in this way scattered radiation was prevented from entering the ionization chamber.

The filament of the tube was maintained at a constant temperature by a set of storage batteries while the potential across the tube was supplied by a 5 KVA high-tension transformer. Since the primary voltage was supplied from the mains small variations of potential across the tube were unavoidable. To make the effect of this variation as small as possible the data were taken in a continuous series of observations lasting over a considerable time. In this way the error due to the fluctuations of potential tended to eliminate itself in the mean of several observations.

The absorption was computed from the following formula,

$$\mu = \frac{2.30}{d} \log_{10} K \frac{T_x}{T_0},$$

where d represents the thickness of the absorber, T_x and T_0 the times required to change the potential of the system to some constant and arbitrary value with and without the absorber and K the fraction of the incident energy transmitted by the empty cell.

RESULTS.

From the data taken the molecular absorption was computed from the relation previously given. The following table gives the results directly obtained from the data for the hydrocarbons.

Compound.	μ.	Molecular Absorption $\times$ 10.^{24}
Pinene, $C_{10}H_{16}$	0.464	1.209
Limonene, $C_{10}H_{16}$	0.457	1.206
Benzene, C_6H_6	0.485	0.707
Toluol, C_7H_8	0.477	0.834

From these different compounds various sets of simultaneous equations may be written and from them the atomic absorption of carbon can be determined. These values for the absorption of the carbon atom together with the different combinations of the compounds used are as follows:

Benzene—Pinene	0.1132×10^{-22}
Benzene—Limonene	0.1137×10^{-22}
Benzene—Toluol	0.1100×10^{-22}
Toluol—Limonene	0.1155×10^{-22}
Toluol—Pinene	0.1148×10^{-22}
Mean =	0.1134×10^{-22}

Knowing the absorption of the carbon atom it was then possible to get the absorption of the hydrogen atom from the molecular absorption of each of the hydrocarbons used. The values obtained for hydrogen from the different compounds are, pinene 0.0050, limonene 0.0045, benzene 0.0045 and toluol 0.0047. In each case the numerics are multiplied by 10^{-22}.

The results obtained for the atomic absorption of oxygen and the compounds from which they were obtained are given below.

Substance.	μ.	Molecular Absorption.	Atomic Absorption of Oxygen.
Isopropyl Alcohol, C_3H_8O	0.544	0.683×10^{-22}	0.304×10^{-22}
Methyl Proprionate, $C_4H_8O_2$	.698	1.089	0.299
Ethyl Acetate, $C_4H_8O_2$	.684	1.099	0.304
Acetone, C_3H_8O	.563	0.679	0.310
Ethyl Tomate, $C_3H_6O_2$	.737	0.970	0.301
Trimethylene Glycal, $C_3H_8O_2$	.833	0.986	0.304

Mean = 0.304×10^{-22}.

A summary of all results obtained by the author and those obtained by others are included in the following table.

Preliminary experiments showed the necessity of specially prepared chemical compounds to avoid the impurities which are often present in materials supposed to be pure. In the preparation of the hydrocarbons the author commenced with relatively pure samples of pinene, limonene and benzene and further purified these through repeated distillation or crystallization. The toluol used was not further purified but since it gave results in agreement with those obtained from the other compounds the results are likewise included in the tables. The oxygen compounds were specimens very carefully purified by Mr. G. A. Ramsdell of the department of chemistry and left little to be desired in their purity.

Substance.	**Observers.**			
	Hewlett.	**Richtmyer.**	**Windgårth.**	**Taylor.**
Carbon, μ/ρ	0.551		0.667	
μ_a*	0.1084[2]		0.1313[2]	0.1134
Oxygen, μ/ρ	1.126		1.000	
μ_a	0.295[3]		2.62[2]	0.304
Hydrogen, μ_a	0.011[1]			0.0048
Aluminum, μ/ρ	5.17	5.32	5.28	5.15
μ_a	2.30[3]	2.37[2]	2.36[2]	2.29
Water, μ/ρ	1.073	1.129	1.013[3]	1.089
μ mol.	.317[3]	0.333		0.322
Acetone, μ/ρ			0.786	0.714
μ mol.			.748[3]	0.679

μ_a* Written for atomic absorption.

The high value obtained by Windgårth for the absorption of oxygen is probably due to an impurity of high atomic weight. The molecular absorption of acetone as determined by that investigator is considerably higher than the value obtained by the writer. Acetone and many other organic compounds absorb moisture from the air and unless used soon after preparation will cause an error depending upon the amount absorbed.

From the data it is seen that two pairs of isomers have been used. Within the limit of the experiment the molecular absorptions are the same for the compounds of the same composition and offer additional evidence in favor of the view that x-ray absorption is an atomic property. In the case of oxygen however there seems to be a difference between the atomic absorption of oxygen as determined by Hewlett using liquid oxygen and that determined from oxygen compounds in this investigation which is somewhat greater than the error of measurements. Whether there is any significance to this small difference can only be determined by additional work in which the same investigator uses both forms of oxygen. Some doubt may also be cast upon the belief that x-ray absorption is a property of the atom only when one considers the absorption of hydrogen as determined in this research. From the measurement of the molecular absorptions of four hydrocarbons the atomic absorption of hydrogen was found to be 0.0048×10^{-22}. When the atomic absorption of oxygen 0.304×10^{-22} is subtracted from the molecular absorption of water, 0.322×10^{-22} a value is found for the absorption of hydrogen approximately twice that as determined from the hydrocarbons. This difference in the absorption of the hydrogen atom seems considerably greater than the experimental error would account for. This apparent difference in the absorption of hydrogen in water and in hydrocarbons might be caused by a difference in the strength of the bond uniting the hydrogen to the other elements of the compound. This seems the most probable when one realizes the extreme stability of the hydrocarbons and the ease with which water is broken up.

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[1] Computed from author's data on water and oxygen.

[2] Computed from author's data.

[3] Computed from author's data from value for $\lambda = .430$ Å. by the relation $\mu/\rho = K\lambda^3 + \sigma/\rho$.

UNIVERSITY OF WISCONSIN,
MADISON, WISCONSIN,
Aug. 5, 1922.

A SECOND UNDAMPED WAVE METHOD OF DETERMINING DIELECTRIC CONSTANTS.

By A. P. Carman and G. T. Lorance.

Synopsis.

New Undamped Wave Method of Measuring Capacities, Changes of Capacity and Dielectric Constants.—A previously described method is very fatiguing, since it involves adjusting a beat tone produced by two ultra-audion circuits, to the same pitch as that of a standard tuning fork. The new method involves merely reading galvanometer deflections, and depends upon the observation that under certain conditions the *relation between current in plate circuit and capacity in the oscillating circuit* is linear for a limited range, therefore three current readings, corresponding to an unknown and two known capacities, are sufficient to determine the unknown. Small changes of capacity, for instance 0.01 cm. in 1000 cm., can readily be detected and measured. The accuracy of the method is practically equal to that of the standards if sufficient care is taken to keep circuit conditions constant.

Dielectric Constant for Air, Carbon Dioxide and Illuminating Gas.—Preliminary results obtained by the above method are 1.00060, 1.00099 and 1.00077, respectively, for 76 cm. of Hg.

IN December, 1919, W. H. Hyslop and the first named of the present writers, presented a paper before the American Physical Society[1] on "An Undamped Wave Method of Determining Dielectric Constants of Liqúids." This method uses two circuits of the "ultra-audion" type, one operating at a constant frequency, and the other tuned by changing the capacity of an adjustable condenser to such a frequency that a definite beat tone is obtained for the two circuits. The beat tone is fixed by the ear, a tuning fork being used as a standard for comparison. A substitution method is then used to determine the capacity of the condenser with and without the dielectric. Later, Professor Whiddington[2] published the account of his ingenious use of ultra-audion circuits to measure minute changes in distance between air-condenser plates by the changes in capacity. Other uses of the same general method have since been independently made.

Recent work carried on by the first writer and his students has shown that while the limit of accuracy of the above ultra-audion method is theoretically only that of the calibration of the adjustable capacity standards, yet practically there is a limit owing to the fatigue of the ear. After an observer has worked a half-hour or so in tuning a circuit with a tuning fork or other tone standard, he is apt to become fatigued and nervous. While we have considerable unpublished data on dielectric constants, determined by the above method, we have on account of this fatigue turned attention to developing a method involving the reading of an instrument rather than the one involving the comparison of tones. The method described below was suggested by Mr. J. J. Dowling's "Recording Ultra-Micrometer,"[1] and has proved sensitive and convenient in use. One arrangement of the circuit used by us is shown in Fig. 1. There is an audion, with an inductance L and capacity $(C_1 + C_2)$ in the grid circuit arranged so as to generate undamped oscillations of any desired frequency. In the plate circuit, there is joined in parallel the adjustable resistance R_s and the galvanometer G. The resistance circuit R_s includes a battery of e.m.f. E_s, and forms what Mr. Dowling calls a "zero shunt," enabling the use of a sensitive mirror galvanometer G to measure changes in the plate current, when R_s is large compared with the galvanometer resistance. We have used a Leeds and Northrup mirror galvanometer with a sensitiveness of 2×10^{-9} amp. per scale division. A number of curves showing the change of mean plate current with changes of the capacity $(C_1 + C_2)$ were drawn. These curves varied for different voltages E_p in the plate circuit and with the degree of coupling. The curve shown in Fig. 2 is the curve with 50 volts in the plate circuit, and the coupling which was found to give the maximum slope at that voltage. It is noted from this that for capacities from 1,000 to 3,500 cm. there is a linear relation between the mean plate current and

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[1] Phys. Rev., Vol. XV., p. 243, 1920.

[2] Phil. Mag., Nov., 1920.

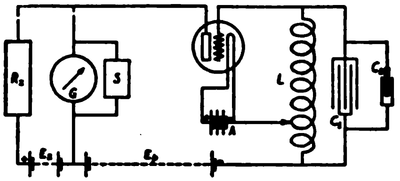

Fig. 1.

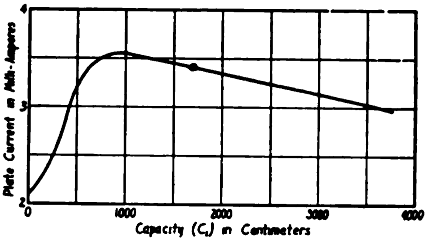

Fig. 2.

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[1] *London Engineering*, Sept. 9, 1921.

the capacity, and a change of 1 cm. corresponds to a change of plate current of 2.1×10^{-7} amperes. It is thus possible to read with the above arrangement a change of capacity of a hundredth of a centimeter. This sensitiveness can be increased by using other e.m.f. of the plate battery and also by using a more sensitive galvanometer, but the above is far more sensitive than called for by the present calibration of our small capacities.

The above method has been tested in the determinations of the dielectric constants of a number of gases. Two "air" condensers were used, the larger one C_1 of a fixed capacity of 3,580 cm. and the smaller one C_2 of adjustable capacity. The construction of these condensers is most easily given by Figs. 3 and 4. The larger condenser is placed in a glass cylinder which is exhausted by a "Hy-Vac" pump, and into which the different gases can be introduced. The whole apparatus is enclosed in grounded wire cages. The eyepiece of the galvanometer projects through a small opening in the wire screen. The capacity of the small adjustable cylindrical condenser is changed from the outside by strings. The function of this condenser is to determine the relation between the galvanometer deflections and the change in capacity. The change in capacity of the "air" condenser in a vacuum and with a given gas as dielectric can thus be measured in terms of deflections of the galvanometer. The results which we have obtained are only preliminary since we have not yet calibrated our small standard condenser with the desired accuracy. We are also not sure of the purity of the gases used, though they are from standard producers, and are supposed to be "pure."

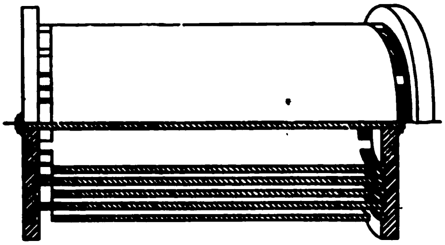

Fig. 3.

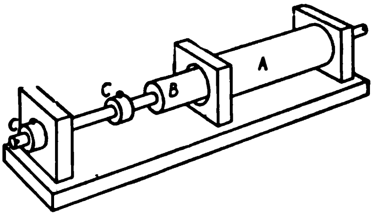

Fig. 4.

Some of the preliminary results are as follows:

TABLE.

Dielectric Constant K for Air.

Change in Pressure in Cms. Hg.	Galv. Deflection for Corresponding Change in C_1.	Galv. Deflection for Calibrating Condenser C_2, Set for 1.5 Cms.	K for 76 Cm. Hg.
0 to 75	3.32	3.00	1.000618
0 to 75	3.20	2.85	1.000627
0 to 75	3.30	3.20	1.000576
0 to 75	3.50	3.35	1.000583
Mean			1.000601

K for illuminating gas at 76 cm. Hg. = 1.000772
K for carbon dioxide at 76 cm. Hg. = 1.00099

The method is so sensitive that any lack of constancy in conditions becomes important. Thus, one of the greatest difficulties was that of maintaining a constancy of the filament current; as a change of temperature of bulb or other part of circuit, or little irregular action of the storage battery changed the filament current and this showed in the mirror galvanometer in the plate circuit. Most of these minor but important difficulties are now reduced or eliminated.

LABORATORY OF PHYSICS,
UNIVERSITY OF ILLINOIS,
URBANA, ILLINOIS,
June, 1922.

ON A NEW METHOD FOR THE GENERATION OF SOUND-WAVES.[1]

By Jul. Hartmann,

Dr. techn. Docent in the Royal Technical College, Copenhagen.

Synopsis.

Pressure variation along a high-velocity air jet, produced by a pressure of 0.9 to 5 atm. above normal, was determined with a simple Pitot tube, and the periodic intervals of instability were located (Figs. 2 and 5).

New Source of Sound; Resonator Actuated by a High-Velocity Air Jet.—It was found that the intervals of instability referred to above can be used for the generation of sound. (1) *Bulb form.* When the small orifice to a bulb is placed in one of these intervals so that the particles of air move in and out of the opening, pulsations like those of a siren are produced, the tones not being pure. The fundamental frequency depends on the volume of the bulb, the size of the orifice and the position in the jet, and may readily be varied from 1/10 to 5,000 per second. (2) *Cylindrical form.* When a simple cylindrical resonator is placed with one end in an interval of instability, pure tones are produced except in certain positions when overtones may be present. The frequency is the fundamental of the resonator and may be made as high as 125,000 per second by using a very short tube, about 0.5 mm. in length and in bore. With a hydrogen jet, the frequencies are, of course, 3.8 times as high. The *efficiency* of such sources is remarkable, intensities that are painful being readily produced. Practical forms of these generators are illustrated (Figs. 3 and 4).

Introduction.

If air is allowed to stream from a container in which the absolute pressure is more than 1.9 atm.—that is the overpressure is higher than 0.9 atm.—through a hole or a short bore out into the free atmosphere, a jet is produced which exhibits a peculiar periodic structure. It was *Mach* and *Salcher*[2] who first noticed this structure by photographing the jet. Mach explained it as due to stationary sound-waves and suggested an explanation as to how the waves were created. Later the jet was studied by R. Emden[3]—also by means of photography—and he produced a theory for the sound-waves. A direct investigation of the distribution of the pressure in the air-jet was carried out by Parenty[4] by means of a sound which was introduced into the jet, and the same method, but with considerably improved apparatus, was employed by

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[1] Extract from "Det kgl. Danske Videnskabernes Selskab. Mathm. fysiske Meddelelser," I., 13, 1919.

[2] Wied. Ann., 41, p. 144, 1890.

[3] Wied. Ann., 69, p. 264 and 426, 1899.

[4] Ann. Chem. Phys., 12, 289, 1897.

Stodola.[1] Stodola's experiments have to a high degree contributed to elucidate the structure of the air-jet. Finally should be mentioned very important work done by Prandtl[2] who succeeded in solving the differential equation for the wave-motion in the jet, and to whom we owe a series of exceedingly instructive photographs of the jet. Thus we now possess a fairly complete comprehension of the air-jet and especially it is now known that the periodical structure is closely connected with the fact of the velocity of the jet, with sufficiently high overpressure, being higher than that of the sound.

THE USE OF THE AIR-JET FOR THE GENERATION OF SOUND-WAVES.

The author has carried out a series of investigations on the jet by means of the arrangement shown in Fig. 1. In this figure, the jet-forming element is indicated by the letter S and is shown as a drawn-out glass tube. K designates the sound of a Pitot apparatus connected through the rubber tube r_1 with one of the branches of the U-shaped manometer M. The other branch of M was, through r_2, connected with the bulb B, from which the air was flowing to S. In B the air was kept at a constant pressure by means of a compressor, which through r_3 communicated with B. In the experiment an air-chamber of about $15l$ was inserted between the bulb B, which had a volume of about $\frac{1}{2}l$, and the compressor.

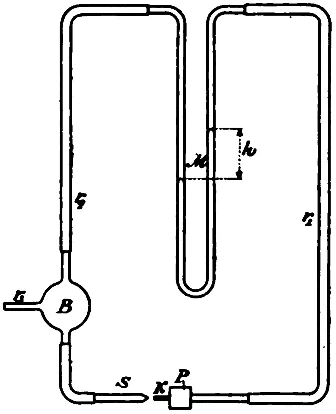

Fig. 1.

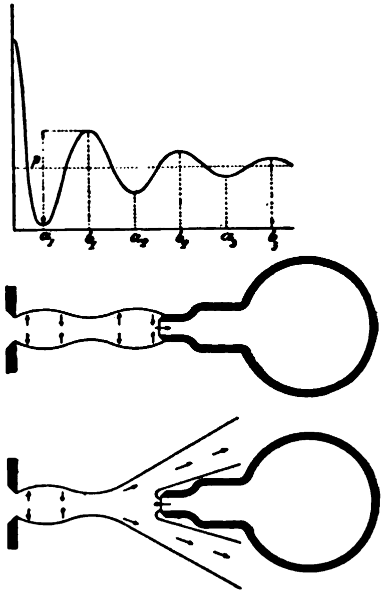

Fig. 2.

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[1] A. Stodola, Die Dampfturbine, Berlin, 1910.

[2] Phys. Zs., 5, p. 599, 1904, and 8, 23, 1907.

In representing the pressure difference h, read on the manometer, graphically for varying positions of the sound K out along the axis of the air-jet one gets a curve of the character shown in Fig. 2, a, provided the pressure in B is lying between the above-mentioned critical and a certain higher value. The curve, as will be seen, gives a picture of the periodical structure of the jet. In comparing the curve with photographs of the jet it is found that the Pitot curve fairly truly represents the pressure-variations along the axis of the jet.

It was now found that the intervals $a_1\,b_1$, $a_2\,b_2$, $a_3\,b_3$ and so on, the intervals of instability as they are termed below, within which the pressure increases, may be used for the production of air-waves of two different types, which will be considered separately in the following. For the production of the one kind of waves a bulb, Fig. 2b, provided with a tube which is drawn out to a fine aperture, can be used. When this aperture is introduced into one of the intervals of instability, as indicated in the figure where the jet is drawn in correct position to the curve in Fig. 2, a, the bulb will periodically fill with, and again exhaust air. The motion of the air particles during the filling and the exhaust is schematically indicated in Fig. 2, b and Fig. 2, c. The period of the phenomena depends on the size of the bulb, on the width of its mouth, on the position of this latter in the interval $a\,b$, and finally on the interval of instability, and on the pressure in that container from which the air flows to the jet. The larger the volume or the smaller the mouth, the longer the period. All periods from, say, 10 sec. or more to 1/5,000 sec. or less can easily be produced. The rapid oscillations of the air are of course heard as a tone. Same has the same unclear character as that of a siren. We shall in the following term the indicated air-oscillations as *pulsations* in order to distinguish them from the other kind of oscillations which may appropriately be called resonance-oscillations. The latter receive their designation from the fact that they are produced by introducing the mouth of a simple cylindrical resonator (oscillator) into one of the intervals of instability. The air will in this case oscillate mainly with the natural frequency of the resonator so that the produced regular sound-waves attain a wave-length of fully four times the depth of the resonator. Thus the frequency is now to a certain degree independent of the interval of instability as well as of the location of the aperture of the resonator in this latter, and of the pressure of the outflowing air, etc. The intensity of the oscillations however undoubtedly increases with the rise of pressure p in the interval of instability. (See Fig. 2, a.) It is ordinarily very high due undoubtedly partly to the high density of the energy in the air-jet, partly to a comparatively very high efficiency of the generator. (Provisory measurements seem to prove that the efficiency at about 20,000 periods per sec. is as high as 10 per cent.) As to the frequency, resonance-oscillations, *i.e.*, pure acoustic oscillations of 100,000 periods per second or more, can easily be produced by means of a jet of atmospheric air. With a jet of hydrogen a frequency of more than 300,000 can be obtained. As a matter of fact the author has been able to produce intense sound-waves of 340,000 periods, and in all probability there will be nothing to prevent the production of still higher frequencies. The author therefore holds the opinion that the air-jet in connection with a resonator furnishes a means for producing intensive, pure acoustic oscillations of higher frequencies than has hitherto been possible.

Practical Forms of the Acoustic Generator.

As to the practical construction of an apparatus for the production of air-waves (pulsations of resonance-oscillations) according to the new principle, numerous possibilities present themselves. What is required is merely a means for inserting the aperture of the resonator or "pulsator" (Fig. 2, *b*) into the interval of instability and to center the aperture in relation to the jet. Fig. 3 shows a construction which is adaptable for many purposes. The pressure-tube is here *T*, which has been extended with the jet-forming element *S*. *T* is carried through the wide bore in the vertical arm *A* which is provided with plane sides. By means of two nuts M_1 and M_2, *T* is fastened to *A*. By loosening one of these nuts the jet-hole may be centered relative to the mouth of the resonator *R* by means of three screws s_1, s_2, s_3, of which only one, s_1, is shown in the figure. The resonator is made as a cylindrical bore, of approximately the same diameter as the jet-hole, at the end of a short piece of metal. The edges of the bore are sharpened as shown in the figure. The resonator, respectively the pulsator is screwed into the end of the micrometer screw *M* and can by means of this be adjusted in one or the other of the above-mentioned intervals of instability of the jet. The screw and the

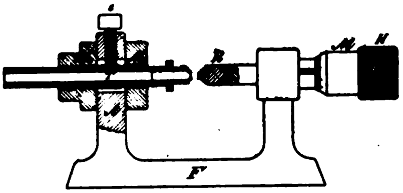

Fig. 3.

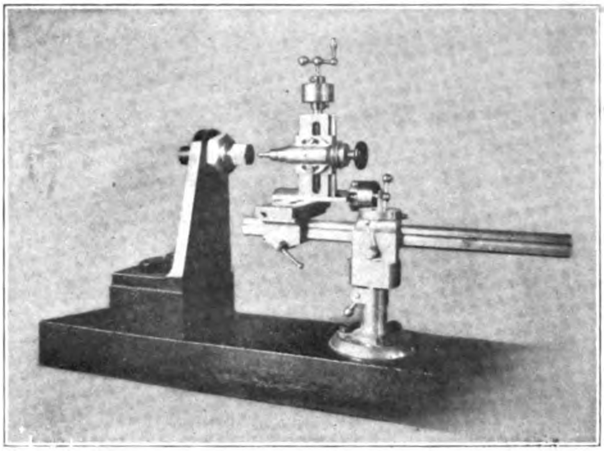

Fig. 4.

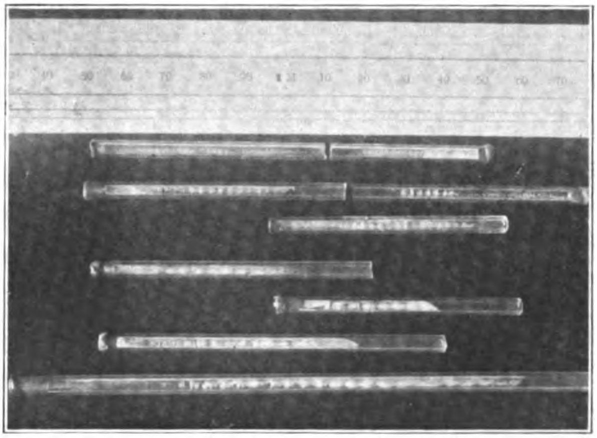

Fig. 7.

JULIUS HARTMANN.

pressure-tube are connected through the baseplate *F* which, if desired, may be attached to a heavier plate or to the apparatus in connection with which the acoustic generator is to be used.

During the fundamental experiments an apparatus was used which has in many respects proved practical. It is shown in Fig. 4. On a heavy iron beam is mounted a vertical stand through which is carried a short pipe. The pipe is at the one end provided with a head into which the jet-forming element is screwed. Another stand on the iron beam carries a horizontal guide rail. On this a combination of three slides may be moved towards or away from the jet-hole. The one slide carries a small chuck in which the resonator can be fastened. By means of two of the slides the resonator can be centered in relation to the jet. By means of the third one the aperture of the resonator can be carried into the interval of instability. Well suited for the jet-forming element is a glass tube drawn out to a short point. Equally suited is a conical bore in a metal plate and this latter form is of course easier to produce. Cylindrical bores are less satisfactory even if they have a conical inlet, as a certain pressure is lost in such bores.

In the event of no compressed-air plant being available, the air for the acoustic generator is taken from a compressed-air bottle. The bottle must of course be provided with a reduction valve. Between this and the generator is preferably inserted an air chamber of a capacity of some liters and provided with a valve by means of which the air supply to the generator may be stopped.

EXPERIMENTS ON THE LOCATION OF THE INTERVALS OF INSTABILITY.

In the following an extract will be given of the experiments, which were carried out as a basis for the new acoustic generator. Fig. 6 represents a curve showing the variation in the readings of the manometer in Fig. 1 out along the axis of an air-jet produced by an over-pressure of 141.0 cm. mercury and by a jet-hole of 0.535 mm. The distances from the jet-hole, measured on a scale, were 100 divisions are equal to 0.275 mm., are shown as abscissæ, and as in Fig. 2, the ordinates represent the difference between the pressure in the container and in the jet. The great regularity in the periodical pressure-variations is especially to be remarked. The approximate location of the intervals of instability is shown in the figure. The second interval extends somewhat out over the pressure-maximum, this is however only due to the uncertainty in the determination of the location. The extension of the intervals of instability was found by means of small "pulsators" made of glass tubes which were at the one end drawn out to a small aperture and at the other end closed by sealing-wax. In the examination of the first interval in Fig. 5, two pulsators of different sizes were used. Each of the two indicated intervals corresponds to its pulsators. The largest interval was found by means of the largest pulsator. The smallest pulsator had a volume of only some few mm.^{3}, the largest was not larger than that its pulsations could be heard as a tone. If the aperture of the smallest pulsator was placed in the first part of the first interval (nearest the jet-hole) it would produce, within the small interval which is denoted in the figure by a double-arrow, a pure tone of about 100,000 oscillations per second.

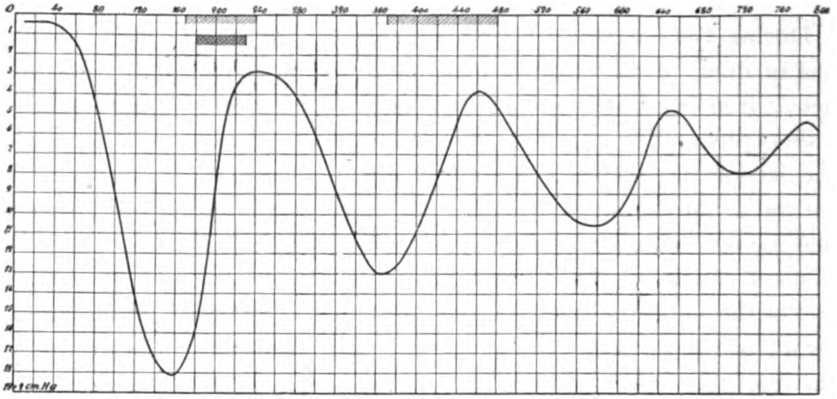

Fig. 5.

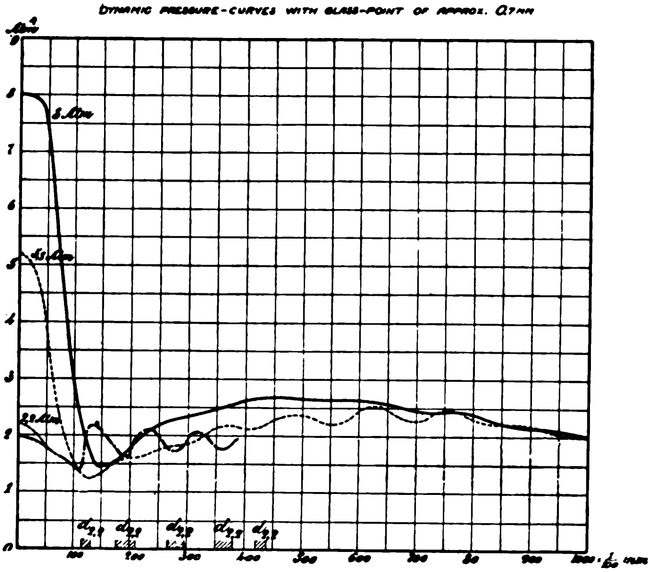

Fig. 6.

The periodical character of the pressure-variations in the jet is only observed for overpressures under a certain limit. Fig. 6 illustrates the changes when this limit is passed. At the lowest overpressure of 2.2 atm., the periodical pressure-variations and the sharply separated intervals of instability $d_{2\cdot 1}$, $d_{2\cdot 2}$, $\cdots$ again occur. Altogether five such intervals have been observed. Undue importance must not be attached to the limits of the intervals, as the determination of same was connected with great uncertainty. When the pressure is increased the intervals by and by are mingled up. At a pressure of 5.2 atm., an interval of instability started at the abscissa 350 and extended to 620. Thereafter followed a smaller isolated interval from 660 to 700. With a resonator (No. 13) which produced a rather high tone, the beginning of the interval of instability was observed as low as 230 and the interval extended to about 900. Possibly there could be traced outside this interval a smaller one between 950 and 1050.

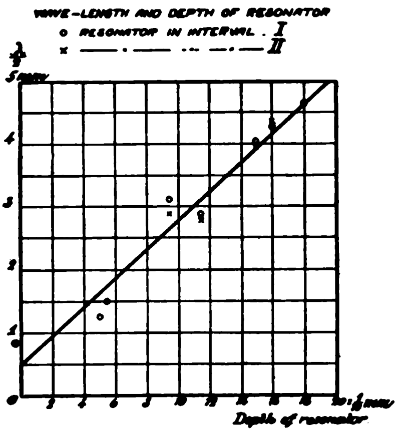

Fig. 8.

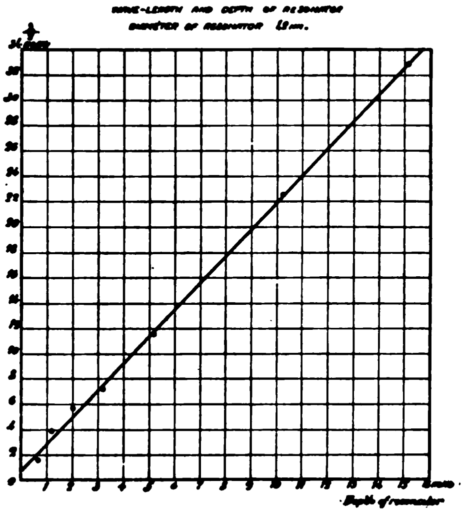

Fig. 9.

Experiments on the Dependency of the Number of Oscillations on the Dimensions of the Resonator.

A number of resonators of the type shown in Fig. 3 were produced. The depth d was measured and it was investigated how the produced oscillations depended on d. The wave-length λ corresponding to the oscillations was measured by means of Kundt-tubes. Samples of the dust-figures are shown in Fig. 7 together with a millimeter scale which makes it possible to determine the length of the waves. In Fig. 8 a curve is reproduced showing the variation of $\lambda/2$ with d, for a number of very small resonators, all of which had an aperture of 0.7 mm. The two series of observations correspond to the two first intervals of instability. The curve is, as will be seen, a straight line. In Fig. 9 are represented the results of a second experiment which was made with deeper resonators of 1.2 mm. aperture. The curve is also here a straight line and may with the units of the figures be represented by the formula:

$$\lambda = 4.22 \cdot d + 1.2,$$
$$\lambda = 4.22\,(d + 0.3).$$

The wave-length is thus, as may be expected, approximately 4 times the depth of the resonator. The divergence from 4 is perhaps due to the fact that the temperature of the oscillating air in the resonator is not the same as that in the Kundt-tube. The constant 1.2 in the first formula indicates the well-known fact that the oscillations in the resonator extend somewhat outside the mouth of the resonator. It is usually assumed that the extension outside the mouth is approximately 0.6 time the radius of the resonator. In the second formula 0.3 should represent this extension in fairly good accordance with that assumed, 0.6 time the radius of the resonator 0.6 being 0.36.

The frequency of the oscillations of the resonator is as already mentioned, mainly determined by the dimensions of the resonator, and especially by its depth. Hereby it is of course assumed that the resonator is always blown with the same kind of air. If a jet of hydrogen is used, the frequency is found to be, as is to be expected and as has already been indicated, about four times as high as with a jet of atmospheric air. For instance the following results were found:

Resonator.	$\lambda/2$ Air.	$\lambda/2$ Hydrogen.	Proportion.	Remarks.
6..........	0.464 cm.	0.130 cm.	3.6	
8..........	0.145 cm.	0.050 cm.	3.0	uncertain
14..........	3.47 cm.	0.925 cm.	3.5	

The proportion between the wave-lengths (measured in the same medium) should be 3.8. If it is perhaps somewhat lower, it may be because the technical hydrogen used was not quite pure.

The intensity of the here-considered resonance-oscillations is, as already stated, very large, notwithstanding the smallness of the resonator. The possibility of making the resonator very small, especially of a small diameter, explains how it comes that the frequency can be made as high as is actually the case. A small diameter means a small value of the constant term in the formula for the wave-length. Now it is obvious that the smaller this term is the smaller values or the higher frequencies can be obtained by diminishing the depth d of the resonator. By way of illustration we may consider a resonator of a depth 0.5 mm. With such a resonator the diameter can at least be made as small as 0.5 mm. The constant term will in this case be

$$\frac{0.6 \cdot 0.5}{2} = 0{,}15 \text{ mm.}$$

Thus the effective depth of the resonator is 0.65 mm. which gives

$$\frac{320{,}000}{4.065} = 123{,}000 \text{ periods per sec.,}$$

the velocity of sound being 320,000 mm./sec. With a hydrogen-jet the frequency would be $3.8 \cdot 123{,}000 = 476{,}000$ periods per sec., thus very nearly half a million per sec. It may be remarked that oscillations of very high frequencies can easily be produced as first overtones of oscillators of greater depth. Some observations are stated in the table below. The first overtone is produced by adjusting the aperture of the resonator right up to that limit of the first interval of instability which is nearest to the jet-hole. In the indicated experiments the highest frequency is, as will be seen, about 120,000 periods per sec.

Resonator.	λ/2 Fundamental Note.	λ/2 Overtone.	Proportion.
22	1.20 mm.	0.400 mm.	3.0
7	0.65 mm.	0.205 mm.	3.2
12	0.49 mm.	0.142 mm.	3.4

The intensity of the resonance-oscillations may be illustrated by the following example. A resonator of about 24,000 periods per sec. and with an aperture of 1.7 mm., was adjusted in an air-jet produced with a bore of 1.5 mm. With an overpressure of 4–5 atm. very good dust-figures were obtained at a distance of about ½ m. from the resonator when a Kundt tube of 4 mm. aperture was used. With a resonator of about 10,000 periods per sec. and with an aperture of 1.5 mm. the produced tone was even with rather small overpressures almost unbearably intensive and left the observer with a physiological after-effect of several hours' duration.

THE ROYAL TECHNICAL COLLEGE,
COPENHAGEN.

ON THE INFLUENCE OF THE SURFACE-TENSION ON THE EFFLUX OF A LIQUID IN JET FORM.[1]

By Jul. Hartmann,

Dr. techn. Docent in the Royal Technical College, Copenhagen.

Synopsis.

Influence of Surface Tension on the Efflux of a Liquid Jet.—Christiansen suggested that surface tension exerts a pressure acting against the pressure causing the flow, so that the Torricelli equation becomes: $v^2 = 2\pi^2\kappa^4 r^4 g(h - h_0)$. If then κ, the coefficient of effective contraction, is constant, v^2 should be a linear function of h, intercepting the $h = 0$ axis at h_0. *Experiments with mercury and water*, in which the speed of efflux was determined down to low values of h, confirm this theory. With cylindrical holes, straight lines were obtained, but with conical holes the relation is curvilinear because of the decrease of the contraction with the speed; yet both types of curve gave the same value of h_0. With water, holes through paraffin paper were used. When the speed decreased to a critical value for each jet, pulsations began to appear but these did not affect the speed of efflux. Photographs are given of various jets. As a qualitative confirmation of the theory, ether vapor, which is known to decrease the surface tension of water, was found to decrease h_0 by 18 per cent.

Jet Method of Measuring Surface Tension.—According to Christiansen the surface tension is equal to $r\rho g h_0$. The measurements with mercury and water confirmed this relation, as after correcting for the loss of head in the cylindrical hole, the values of the surface tension came out 536 dynes/cm. for Hg at 16° C. and 74 dynes/cm. for water at 10° C., within one per cent. of the accepted values. It is believed the method is capable of higher accuracy, if developed.

Introductory.

An influence of the surface-tension on the efflux of a liquid in jet form has long ago been recognized. But the manner in which the tension acts has very often been highly misunderstood. Thus, when, from a certain orifice at a certain head, there flows per sec. a greater volume of a liquid with a smaller surface-tension than of a liquid with a larger one, this fact has been accounted for by the supposition of the surface-tension in the latter case tightening the jet to a greater extent and thereby increasing the contraction. For instance this explanation will be found in Jamins's textbook, Cours de Physique, Vol. I. Possibly it has from there or from the source used by Jamins found its way into other textbooks. I give Jamins's representation of the matter:

"*Girard*[2] avait déjà constaté que l'alcool coule plus rapidement que l'eau à travers des orifices percés en mince paroi: la section contractée de la veine doit donc être plus grande pour l'alcool que pour l'eau, et c'est en particulier ce qui résult de mesures directes de *M. Isarn.*[1] Il suffit, d'après ce dernier savant, de vaporiser de l'alcool ou de l'éther à peu de distance d'un orifice par lequel l'eau s'écoule, pour que, le liquide à faible tension superficielle se disolvant dans l'eau, la dépense de l'orifice augmente dans une proportion appréciable."

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[1] Extract from the report in Det kgl. Danske Vidensk. Selsk. Math.-fysiske Meddelelser' II., 8, 1919.

[2] Girard, Mémoires de l'Académie, T. I., 1816.

Probably the first to propound the explanation which according to the investigation described in the following is the true one, is the late Professor C. Christiansen.[1] The surface-tension being C, there must, in the opinion of Professor C. Christiansen, exist, in a cylindrical jet with radius r, a pressure C/r which counteracts the efflux and which must be subtracted from the pressure under which the liquid flows out, when on the basis of Torricelli's principle it is desired to calculate the quantity of liquid leaving the orifice. Professor C. Christiansen endeavored to carry through the investigation which has now been executed by me, but his attempt was unsuccessful and indeed the result could not well be otherwise in view of the imperfect apparatus utilized. The author took up the experiments mainly because they promised a simple method for the measurement of surface-tensions and because it could not a priori be taken for granted that Professor Christiansen's view of the influence of the tension was incontrovertibly correct. The result has been a complete verification of Professor Christiansen's hypothesis in that the determination, on basis of same, of the surface-tension for water and mercury has given values for these physical constants practically consistent with the best hitherto obtained. After having substantiated this the author has, on basis of the experiments, worked out a new method for the determination of the surface-tension.

Research apparatus.

The research apparatus shown in Fig. 1, *a–c*, consisted of a cylindrical cast-iron basin with an inside diameter of 14.845 cm. and a depth of about 9.5 cm. On opposite sides of the basin were placed two stiffenings, *F*, with plane outsides. Through each of these and the wall of the cylinder two bores were carried, Fig. 1, *c*. One of these in each stiffening was intended for a window, *V*. In the second bore in one of the stiffenings the jet-forming element *P*—the hole-plate—was screwed. The corresponding bore in the second stiffening was not utilized and was therefore closed by a plug.

In the experiments it is necessary to be able to open and close the jet-hole rapidly. The lock is shown in Fig. 1, *a*; it was fixed on the plane front of the stiffening *F'*. From *F'* it was insulated electrically by means of the fiber disc *I*. To this the short horizontal arm A_1 was attached. To A_1 again the vertical arm A_2 could be fixed by means of the screw *K*, so that the arm and what was attached to it could easily be removed when

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[1] C. Christiansen, Ann. d. Phys., 5, 436, 1901.

Fig. 1 *a*.

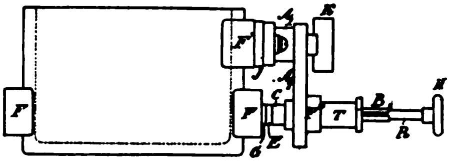


Fig. 1 *b*.

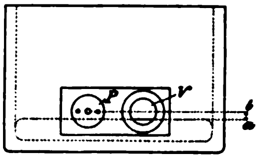
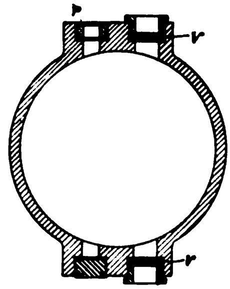


Fig. 1 *c*.



the hole-plate had to be changed. A_2 had below a stiffening *F''*, in which the lock itself could be moved to and fro and fixed in an appropriate position. The lock consisted of a steel disc *E* at the end of the solid cylinder *C*. The edge of *E* was provided with a plain rubber ring, fitting into a groove cut in *E*. When the lock was shut the ring was pressed against the plane foreside of the jet-hole plate. The pressure was exerted by a strong spring placed inside the hollow cylinder *T*. The drawing of the rod *R* outwards, by means of a handle, *H*, opens for the liquid. By means of the bayonet arrangement *B* the lock device, after having been drawn out, could be kept open. Finally it could be closed by a short turn of the handle *H*.

The reason why the lock has been insulated from the basin was that, in other experiments, not dealt with in this paper, it was necessary to transmit an electric current through the jet The disc *E* thereby was to serve as one of the electrodes. The apparatus described was used in the following manner. In the basin was poured 250 cm.^{3} of the liquid with which the experiment was to be carried out. The surface of the liquid formed a bottom in the basin and the depth of this bottom below the center of the jet-hole was measured by a cathetometer with an accuracy of about 0.05 mm. After this a further 1250 cm^3. of the liquid was poured into the basin. The inside diameter of the latter having been measured—also by the cathetometer—the head of the surface of the liquid above the center of the jet-hole could be calculated. The experiment of efflux now consisted in the observation—by means of a stop-watch—of the time of efflux for a series of equal volumes—50.2 cm.^{3}—of the liquid. Of these observations the values of the volume V which flowed out per second were calculated and were written in a table together with the corresponding values of the head. The latter had been calculated once for all under the supposition that each of the tapped-out portions was 50.2 cm.^{3} and furthermore under the assumption that the center of the jet-hole was situated 0.185 cm. above the liquid bottom. If the latter height had a different value a correction was introduced for the "zero error." On the other hand no correction was used for the small oscillating deviations from the value 50.2 cm.^{3} of the tapped-out portions. The average heads were calculated as the simple means of the heads of the surface before and after the efflux of the corresponding liquid portion. The error hereby committed is given by the expression

$$\Delta h = \frac{h_1 + h_2 - 2\sqrt{h_1 h_2}}{4}$$

h_1 resp. h_2 being the effective heads before and after. However in practically every case this error could be ignored. The table finally was reproduced in a $V^2 - h$ curve, *i.e.*, a curve which for abscissæ has the head h, for ordinates the square V^2 of the liquid volumes emitted per second. The head corresponding to the counterpressure of the surface-tension being denoted by h_0, the value of V given by Torricelli's law will be

$$V = \frac{\pi}{4}\kappa^2 \cdot d^2 \cdot \sqrt{2g(h - h_0)},$$

κ being the *coefficient of efflux* or the *coefficient of the effective contraction* and d being the diameter of the jet-hole. Thus the equation of the $V^2 - h$ curve should be

$$V^2 = \left(\frac{\pi}{4}\kappa^2 d^2\right)^2 \cdot 2g \cdot (h - h_0)$$

and so, if κ is a constant, the $V^2 - h$ curve should turn out to be a straight line, which if the h-axis cuts off the length h_0 of which the surface-tension

C, according to Professor Christiansen, can be calculated by the expression

$$h_0 = \frac{2C}{d'\rho g},$$

d' denoting the diameter of the jet and ρ the density of the liquid.

A. Experiments with Mercury.

Alternations in the Aspect of the Jet During the Efflux.

As the surface sinks in the basin during the experiment of efflux the jet of course declines more and more. At the same time its surface will—as long as the head of the liquid still remains above a certain limit—appear more and more smooth. Towards the end of the efflux the jet assumes an aspect, which to some degree depends on the diameter of the jet-hole. With wider bores, for instance bores of 2 mm. and upward, the jet continues to be smooth, and forms, almost to the moment when its velocity is nought, a continuous jet of several cm. length. Fig. 2, *a*, shows a photograph of such a jet produced by means of a jet-hole in carton of 1.96 mm. thickness. Immediately before the cessation of the efflux the long jet suddenly becomes unstable and the efflux hereafter takes place in a marked pulsating manner, the jet which is now quite short assuming a glimmering aspect. With somewhat narrower bores—for instance of 1.2 mm.—the instability occurs at a greater head. With bores of a diameter of about 1.4 mm. a peculiar phenomenon may be observed, the jet changing suddenly from the smooth to the pulsating form and later on reverting to the smooth again. Fig. 2 *b*, shows a photograph of a "jet" of 1.432 mm. during the pulsating efflux. With very narrow bores of a fraction of a millimeter the pulsating form of efflux becomes extremely marked, the mercury ultimately trickling from the jet-hole in small drops.

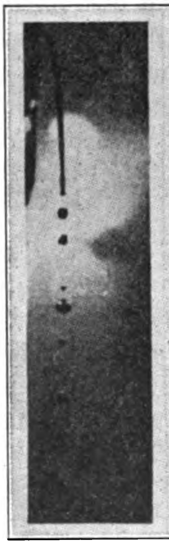


Fig. 2 *a*.

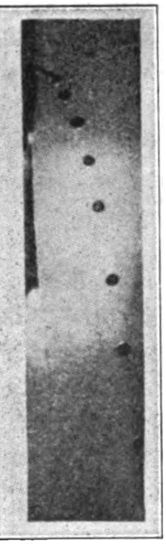


Fig. 2 *b*.

It appears from the investigation that the $V^2 - h$ curve with cylindrical bores is rectilinear down to the smallest heads. The transition from smooth to pulsating jet does not alter the direction of the line essentially but if the efflux takes the form of drops this is easily seen from the $V^2 - h$ curve as Fig. 3 will illustrate. The average pressure, due to the surface tension inside the mercury drops, being smaller than the corresponding pressure inside a jet with a diameter equal to that of the bore, more mercury will flow out in the case of drops than in the case of a jet.

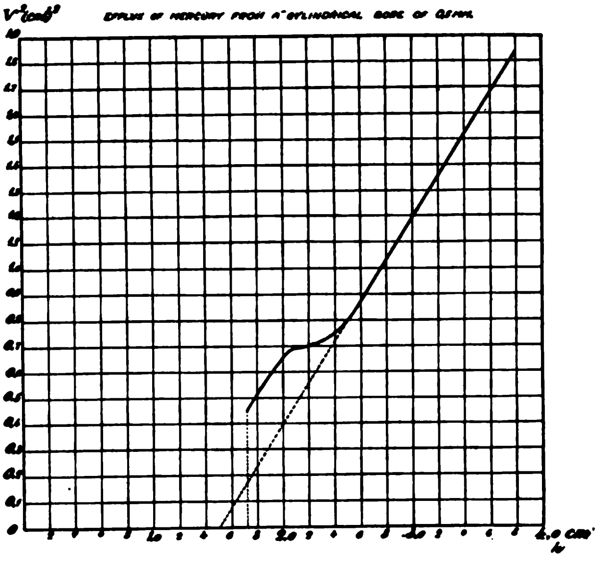


Fig. 3.

Therefore when the phase of drops commences, the $V^2 - h$ curve will to begin with take an upward bend, thereafter falling smoothly owing to the diminishing head.

The Cessation of the Efflux.

When the head has reached a certain lower limit the efflux suddenly ceases and the mercury in the jet-hole will assume a curved surface as shown in Fig. 4. The tension in this surface now supports the remaining mercury-column h_0'. Determinations of h_0' were made for a series of bores, partly of the conical, partly of the cylindrical type, and it was found that the certainty of the measurement of h_0' was very considerable. By way of illustration the following repeated values of the last tapped-out portion in four experiments, carried out with the jet-holes indicated over each of the four last columns, are given below.

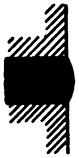


Fig. 4.

In the experiments the last portion after having been measured was poured back into the basin for a new measurement. The uncertainty seems to be abnormally great in the second experiment and yet it is here as low as 3 cm.^{3}. This means that the head at which the efflux ceases is determined by one single observation with a certainty of about 0.16 mm. In the other experiments the certainty is essentially greater.

No.	0.80. 90°	0.93. 90°	2.0. 90°	1.5 cyl.
1......	9.2 cm.^{3}	43.5 cm.^{3}	1.7 cm.^{3}	7.8 cm.^{3}
2......	8.5	40.1	1.7	6.7
3......	8.2	42.5	1.9	6.7
4......	8.8	45.0	1.6	—
5......	—	—	2.1	—
Mean .	8.7 cm.^{3} Δ=0.5 cm.^{3}	42.8 cm.^{3} Δ=2.7 cm.^{3}	1.8 cm.^{3} Δ=0.2 cm.^{3}	7.1 cm.^{3} Δ=0.7 cm.^{3}

Provided the surface of the liquid in the bore, Fig. 4, is spherical with a radius of curvature r', r' will be given by

$$\frac{2C}{r'} = h_0' \cdot 13.55 \cdot 981,$$

C indicating the surface-tension of mercury. Assuming r' to be proportional to the radius r of the bore so that $r' = kr$, then in tracing the variation of h_0' with $1/r$ or $1/d$, d being the diameter of the jet-hole, one should get a straight line. In Fig. 5 all observed values of h_0' are marked

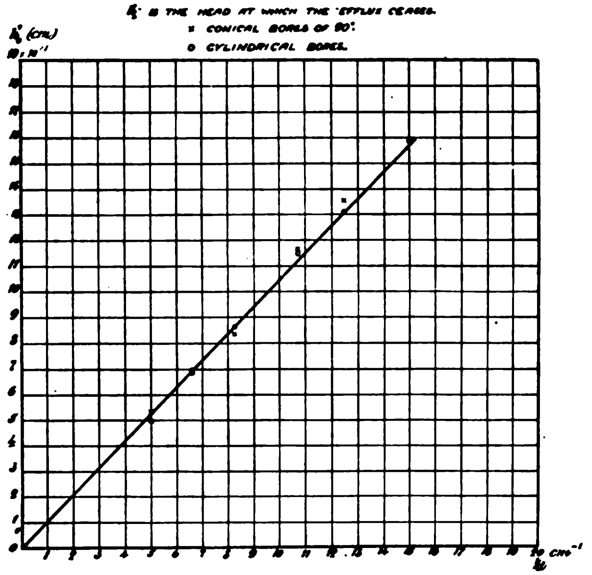


Fig. 5.

in their dependency on $1/d$. Ignoring the value corresponding to the bore with the diameter 0.53 mm., which bore also showed anomalism, with regard to the conditions of efflux, considered above, all the points of observation are distributed with great regularity on both sides of a straight line through zero. From this line one derives for the constant k the value 1.496, when the value 520 dyn./cm. is used for C. *Thus mercury assumes in the jet-hole a radius of curvature which with a fair degree of accuracy is equal to 1/50 times the radius of the bore. And the radius of curvature is quite independent of whether the bore is of the cylindrical or of the conical type.*

The Extrapolated Zero-head and its Connection with the Surface-Tension.

According to Professor Christiansen's view the length h_0, the extrapolated zero-head, which the extended $V^2 - h$ curve cuts off the axis of abscissæ is, as indicated above, determined by

$$\rho g h_0 = \frac{2C}{d'}$$

in which d', as will be remembered, denotes the diameter of the jet. The results of the experiments here described were, briefly, the following. With *cylindrical bores*, the $V^2 - h$ curve is rectilinear, Fig. 6. If extended down to the axis of abscissæ it cuts off from the same length h_0, which, introduced in the formula above, always gives the same value for C, when d' is replaced by the diameter d of the jet-hole—in accordance with the fact of the actual contraction with cylindrical bores being nought. With *conical bores* the $V^2 - h$ curve is curvilinear, Fig. 7. If

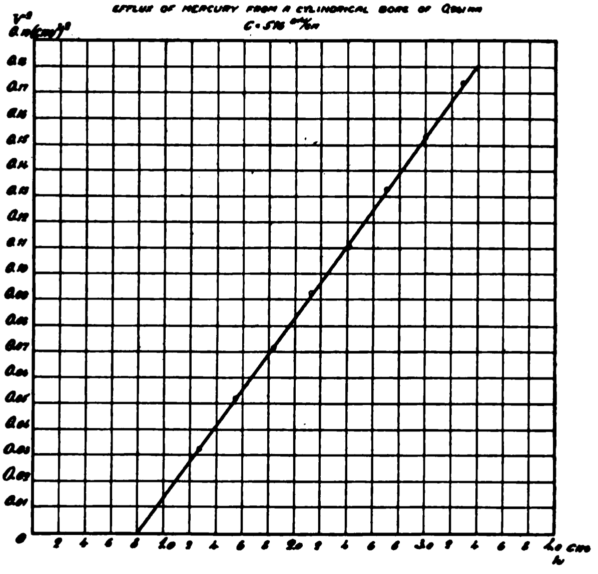


Fig. 6.

extended to intersection with the axis of abscissæ by means of a flexible ruler and if the portion cut off is introduced in the formula for h_0 and if furthermore d', as in the case of the cylindrical bores, is replaced by the diameter d of the jet-hole,—*corresponding to the fact that the actual contraction with decreasing velocity tends to zero*[1]—one again obtains for C a constant value and mainly the same as with cylindrical bores. The common C-value very nearly coincides with those determinations of the surface-tension of mercury considered for the present time as the most reliable.

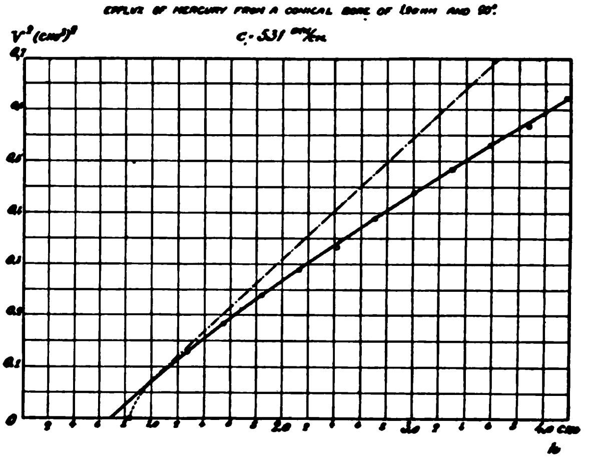


Fig. 7.

In order to illustrate how exactly the $V^2 - h$ curve, both at jets with and without contraction, passes through the point of the axis of abscissæ corresponding to the surface-tension C a series of values for this latter constant found in the course of the investigation is given in the following table.

TABLE I.

No.	Diameter of the Jet-hole.	Length of the Cylindrical Part of the Bore.	C.	Comment.
5.......	0.799 mm.	2.0 mm.	506 dyn./cm.	Cylindrical bores in steel. The C-values have been corrected for the drop of pressure in the cylindrical part of the bores. (See below.)
4.......	0.961	1.2	516	
6.......	1.218	3.0	527	
9 and 10.	1.507	2.5	507	

Mean, 514 dyn./cm. at about 15°.

---

[1] The statements concerning the contraction reproduce the results of a series of experiments carried out by the author.

TABLE II.

No.	Diameter of the Jet-hole.	Thickness of the Carton.	C.	Comment.
85......	1.228 mm.	0.25 mm.	530 dyn./cm.	Holes pressed in carton, Fig. 8. The jet shows a variable contraction.
91 *A–B*..	1.923	0.13	547	
93......	1.228	0.25	548	
94......	0.965	0.13	532	
95......	0.952	0.13	540	
96......	1.380	0.13	522	

Mean, 536 dyn./cm. at about 16°.

As will be seen from the numbers of the experiments the figures in the first table represent results from some of the very first determinations, and these must be regarded exclusively as orientative. On the other hand the second table contains the latest and final determinations of the whole series of experiments. The true value of the surface-tension at 20° of a fresh mercury surface seems to be about 540 dyn./cm. In order to illustrate the accuracy which was reached in the later experiments No. 94 is reproduced in Fig. 9 diminished linearly in the ratio of about 3 to 1.

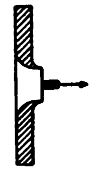


Fig. 8.

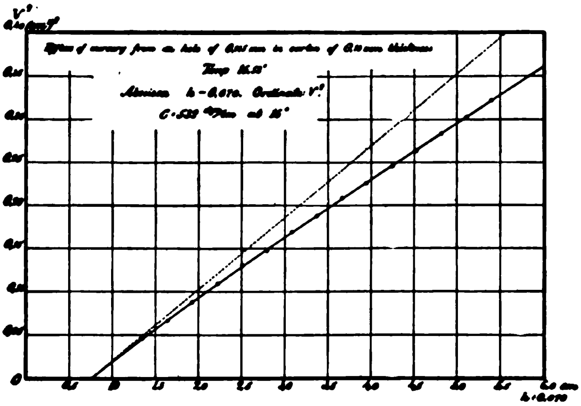


Fig. 9.

B. EXPERIMENTS WITH WATER.

Conditions of Experiments. Changes in the Aspect of the Jet During the Efflux. Cessation of the Efflux.

With a jet-hole in metal or glass it is impossible to carry out a unique experiment of efflux at low head with water or practically any other liquid. This is due to the liquid wetting the surface of the hole-plate. A quantity of liquid accumulates around the jet-hole assuming the form indicated in Fig. 10. With heads of 3–4 cm. a jet is pressed through this mass and the jet stands with a sharp and smooth surface, but the liquid volume flowing out per sec. may vary several per cent. owing to the accidental variations in the form of the liquid mass. And it can be several per cent. larger than the volume which would flow out at the same head if the jet stood with a sharp edge against the hole plate. At a somewhat lower but still at a relatively high pressure the efflux in the form of a jet entirely ceases, the water draining down along the vertical surface of the hole plate. The adhesion of the water to the hole plate thus practically renders impossible the observation of the lower part of the normal $V^2 - h$ curve, and as a consequence hereof also the extrapolation to the zero-head h_0.

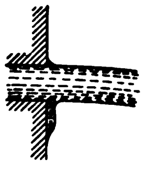


Fig. 10.

But it is possible to carry out practically just as reliable experiments with water as with mercury when, in the case of the first liquid, paraffin, or what is still better, paraffined paper, is used for the production of the hole plate. Water behaves in precisely the same manner towards paraffin as mercury towards iron. Thus a complete experiment of efflux is possible and during such an experiment quite the same variations are observed in the appearance of the jet as is described above for the mercury jet. Particularly distinct is the abrupt transition at low pressures from a long smooth jet to the pulsating form of efflux which again at a still smaller head alters to a smooth jet. Fig. 11, *a–c*, represents instantaneous photographs of the three consecutive phases of the efflux. Fairly characteristic is the abrupt manner in which the continuous part of the jet ends in the case of pulsating efflux. When the head sinks under a certain limit the efflux in form of a jet ceases and hereafter the water drains down along the wall of the hole plate. At a still smaller head h_0' the efflux suddenly stops and the water now stands with a convex

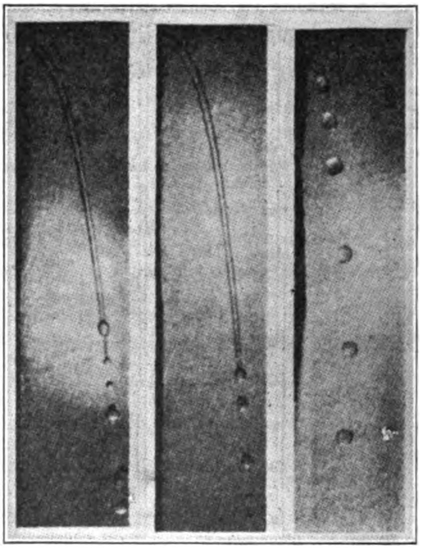


Fig. 11, *a–c*.

surface across the aperture of the jet hole, just as in the case of mercury. The certainty with which h_0' can be measured is, however, not so great with water as with mercury. Thus in one case the following repeated values of the last observed tapped-out portion were found

$$29.4 - 24.5 - 38.4 - 40.8 \text{ cm.}^3.$$

It seems that a systematic variation appears in this series. Four experiments gave for h_0' the values indicated in the following table:

Experiment.	**Radius r of the Bore.**	h_0'.	r'.	r'/r.
No. 61..........	0.735 mm.	1.318 cm.	1.137 mm.	1.55
74..........	0.885	1.051	1.427	1.61
63..........	0.901	0.945	1.590	1.76
73..........	1.091	0.713	2.064	1.89

In the table r' denotes the radius of the convex surface calculated from the expression

$$\frac{2C}{r'} = h_0'g,$$

in which for C—the surface-tension of the water—the value 73.6 dyn./cm. has been used.

The ratio of r' and r, the radius of the jet-hole, increases, as will be seen, with the radius of the jet-hole. The wider the hole is the more flat the curved surface seems to be. The experiments Nos. 61 and 63 were carried out with cylindrical bores in solid paraffin, Nos. 73 and 74 with holes pierced in paraffined paper.

The Zero-head and the Surface-tension.

The result of the test of Professor Christiansen's assumption was for water quite the same as for mercury. The extrapolated zero-head, h_0, determines the surface-tension of water when introduced into the expression $\rho g h_0 = 2C/d'$ given above when d' in this expression is put equal to the diameter d of the jet-hole. The certainty with which the surface-tension can be measured appears from the following summary of some of the determinations.

The experiments of Table I. must be regarded as to some degree orientative. In the experiments of Table II. the sources of error were examined with care and as to Table III. the numbers herein represent

TABLE I.

Experiment.	d.	C. Distilled Water.	C. Water from the Pipes.	Comment.
No. 32.....	1.019 mm.	74.8 dyn./cm.	—— dyn./cm.	Short cylindrical bores in paraffin with conical entrance.
30.....	1.220	74.4	——	
33(26)..	1.591	75.2	75.3	
34(25)..	1.996	70.0	70.0	
31.....	2.211	73.0	——	

Mean, 73.5 dyn./cm. at about 10°.

TABLE II.

Experiment.	Length of the Bores.	d.	C Uncorrected.	C Corrected.	Comment.
No. 57 ..	0.5 cm.	1.616 mm.	70.7 dyn./cm.	70.2 dyn./cm.	Cylindrical bores in paraffin. The inner edge rounded.
58 ..	0.2	1.567	77.1	71.1	
59 ..	0.1	1.698	80.3	72.3	
60 ..	0.4	1.442	88.5	72.9	
61 ..	0.8	1.470	101.3	72.6	
62 ..	0.8	2.490	96.0	73.9	
63	0.8	1.801	90.7	70.5	

Mean, 71.8 dyn./cm.

Corrected for different faults: 74.8 dyn./cm. at about 10°.

TABLE III.

Experiment.	Thickness of the Hole-plate	d.	C.	Comment.
No. 108....	0.17 mm.	1.628 mm.	72.8 dyn./cm.	Holes pierced in paraffined paper. Inner edge rounded.
118....	0.17	1.624	74.8	
111....	0.17	1.878	74.4	
109....	0.38	1.868	74.1	

Mean 74.0 dyn./cm. at about 10°.

the latest and presumably best of all the measurements. As will be seen, all *C*-values are situated very close to 74.0 dyn./cm., *i.e.*, the value which ordinarily is considered the true one for the surface-tension of water at 10°. Other series of experiments were carried out which mainly gave the same result. The series Nos. 49–55, carried out with cylindrical bores with conical entrance, gave for *C* the value 72.4 dyn./cm. at 10°. The series Nos. 71–74*b* (8 determinations at largely varying temperatures) gave $C = 73.4$ dyn./cm. at 10°. Finally from the isolated experiment, No. 69, the value 75.2 dyn./cm. at 10° was found by means of curvilinear extrapolation.[1] In order to show with what degree of certainty the $V^2 - h$ curve could be determined in these experiments, and besides to illustrate the extrapolation carried out,—experiment No. 108 is reproduced in Fig. 12.

Thus water, as far as the question of the relation between h_0 and C is concerned, gave quite the same result as mercury. *The counter-pressure of the surface-tension is directly measured by* h_0.

The Friction-loss in a Longer Cylindrical Bore.

In Table II. above, heading the last column, a correction is indicated which will now be explained. In the preceding column the values of C which are directly evaluated from the $V^2 - h$ curves are reproduced. As will be seen, these values are as a whole too high and increasing with the length and narrowness of the cylindrical bore. In all probability the reason for this must be sought in the friction of the water in the bore and the author tried to calculate a correction for the error based on the assumption that the friction in the bore is equivalent to a loss of pressure h_p which might be evaluated by means of Poiseuilles's expression, *i.e.*, by

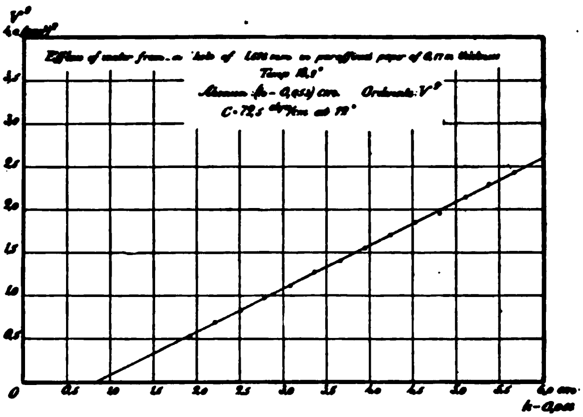


Fig. 12.

$$h_p = \frac{128 \cdot \eta \cdot L}{\pi d^4 g} \cdot V,$$

where η is the coefficient of the viscosity of water at the temperature of the experiment, L the length of the bore and V the volume of liquid which flows out per sec.

---

[1] Holes pierced in paraffined carton ordinarily gave a rectilinear $V^2 - h$ curve. In the experiment No. 69 the carton was rather thin and the internal edge probably has been fairly sharp, so that an actual contraction has been present.

The volume V should accordingly be given by

$$V = \frac{\pi}{4}\kappa'^2 d^2 \cdot \sqrt{2g(h - h_0 - h_p)}$$

instead of by

$$V = \frac{\pi}{4}\kappa^2 d^2 \sqrt{2g(h - h_0)}$$

I now reduced the actual $V^2 - h$ curve to that which would have been observed if h_p had not existed. The reduction was carried out as indicated in Fig. 13. The values of h_p were calculated for two or three points and the abscissæ of these points were diminished by the h_p values. The original $V^2 - h$ curve which was in the main rectilinear or which perhaps had a hardly perceptible downward bend was thereby changed into a new, almost rectilinear but somewhat steeper $V^2 - h$ curve, the rectilinear extension of which cuts off an interval from the axis of abscissæ given, as will be seen from Table II., by

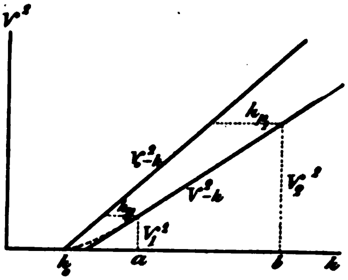


Fig. 13.

$$\frac{2C}{d} = h_0 g.$$

In the calculation of h_p the value of η corresponding to a parallel flow of the liquid is used. In order to give an idea of an experiment treated in the manner here described the experiment No. 60 is shown in Fig. 14.

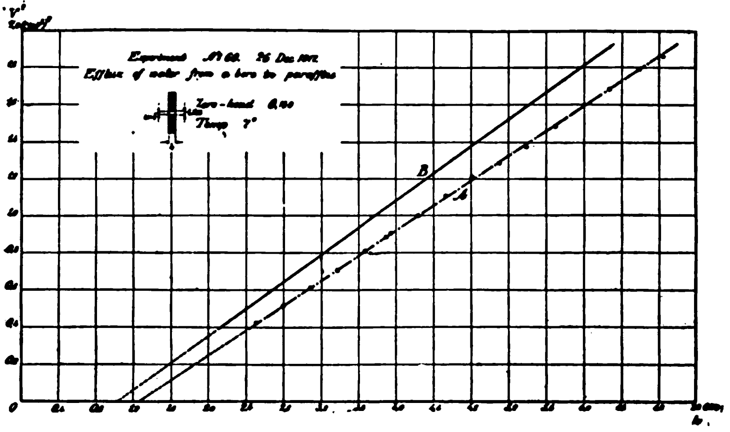


Fig. 14.

On the Influence of Ether vapor on the Surface-tension of Water.

The author found it worth while to repeat the old well-known experiment on the influence of ether vapor on the surface-tension of water. In the experiment a short cylindrical bore with a diameter of 1.278 mm. in solid paraffin was used. The experiment was carried on in such a way that the time of efflux for each of the normal portions of 50.2 mm.[3] was observed on the jet being emitted into air, and also when a small piece of cotton saturated with ether was placed just above and close to the jet. In Fig. 15 the result of this double experiment is shown. It will be noticed that the $V^2 - h$ curve with ether vapor is exactly parallel to the curve with pure air. This suggests that the effect of the ether vapor is almost instantaneous, otherwise it would hardly be immaterial whether the jet has a velocity of 30 cm./sec. as is the case in the lower points of the curve—or 60 cm./sec. as is the case of the higher. Moreover, it will be observed that the uncertainty of the points is not greater with ether vapor than with pure air. This makes it probable that it is the maximum effect of the ether vapor which is dealt with, *i.e.*, the effect which in all probability should be observed at the efflux into an atmosphere of pure ether vapor. The change of the surface-tension amounts, as will be seen, to 18 per cent. It is of course most pronounced with the smallest velocities of the jet. Here the effect is extremely striking and

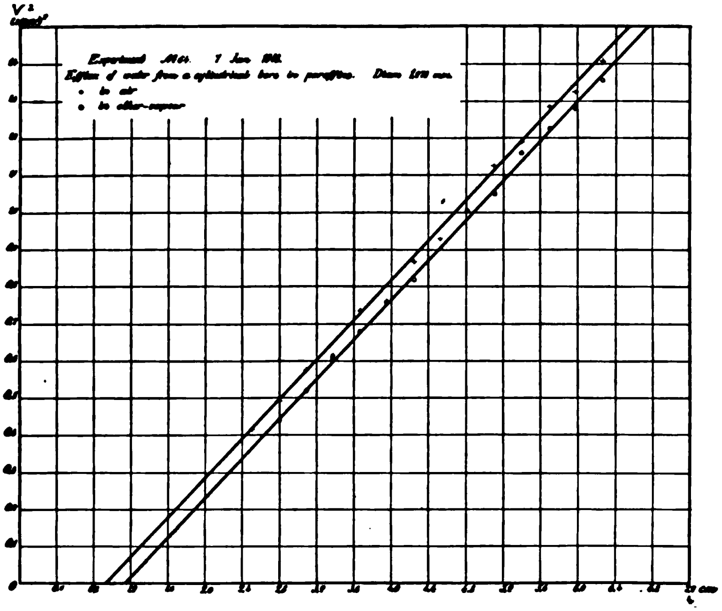


Fig. 15.

can easily be demonstrated in the following way. When the jet in air assumes the pulsating form described above it is observed on introducing the ether vapor that it straightens out and changes into a perfectly smooth and continuous jet, indicating that the counter-pressure of the surface-tension has partly been removed.

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Index to Volume XX, Series II.

A.

Absorbing Media, Electromagnetic Waves in, *Leigh Page*, 166.

Absorbing Medium, Specific Intensity of Radiation in an, *Leigh Page*, 163.

Absorption, Characteristic X-Ray, in the "L" Series for Elements N62 to N77, *J. M. Cork*, 81.

Absorption Coefficients for Homogeneous X-Rays, *E. G. Taylor*, 709.

Absorption, The Effect of a Magnetic Field on the, of X-Rays, *Joseph A. Becker*, 115.

Absorption, The Effect of Certain Dissolved Substances of the Infra-red, of Water, *J. R. Collins*, 486.

Absorption, The Effect of the Magnetic Field on the, of X-Rays, *Joseph A. Becker*, 134.

Absorption, The, of Light by Sodium Vapor, *George R. Harrison*, 198.

Acidity, The Relative Deposition of Radium and Barium Salts as a Function of Temperature and, *W. B. Pietenpol*, 199.

Acoustic Wave Filters, *G. W. Stewart*, 528.

Adiabatic Invariants, A General Method of Determining the, of Mechanical Systems, *V. F. Lenzen*, 201.

Adsorbed Gas, A Study of the Effect of, on the High-Frequency Resistance of Copper Wire, *Austin Bailey*, 154.

Adsorption-Layer Theory, A Transition of, of the E.M.F. of the Voltaic Cell, *R. D. Kleeman*, 174.

Ageing Effect, On the, in the Mobility of Positive Gas Ions, *H. B. Wahlin*, 267.

Air-Gaps, Electrical Conduction Across Minute, *James W. Broxon*, 476.

Air, On the Nature of the Negative and Positive Ions in, Oxygen and Nitrogen, *Henry A. Erikson*, 117.

Alkali Metal Vapors, Radii of the Atoms of the, *S. H. Anderson*, 200.

Alkali Halides, Precision Measurements of the, *Wheeler P. Davey*, 83.

Alloys, The Optical Constants of Sodium-Potassium, *Raymond Morgan*, 204.

Alumina, Cathodoluminescence of Heated, *D. T. Wilber*, 101.

Aluminum. Note on the Ratio of Mass to Weight for Bismuth and, *H. A. Wilson*, 75.

American Physical Society: Abstracts, 81, 195. Minutes, 78, 194.

Analysis of Soils, A New Method of Mechanical, *D. S. Jennings*, *M. D. Thomas* and *Willard Gardner*, 196.

Anderson, S. H., Radii of the Atoms of the Alkali Metal Vapors, 200.

Antennas, The Calculation of the Capacity of, *Frederick W. Grover*, 92.

Arc, Theory of Ionization by Cumulative Action and the Low Voltage, *Karl T. Compton*, 283.

Arcing Voltage, The Effect of Liquid Surface upon the, on Mercury Vapor, *Y. T. Yao*, 105.

Aster, A. K., The Optical Properties of Molten Metals, 349.

Atomic Constants and Dimensional Invariants, *A. C. Lunn*, 1.

Atoms, Radii of the, of the Alkali Metal Vapors, *S. H. Anderson*, 200.

B.

Babbitt, B. J., The Effect of a Longitudinal Magnetic Field on the Mechanical Properties of a Vibrating Nickel Wire, 91.

Bailey, Austin, A Study of the Effect of Adsorbed Gas on the High-Frequency Resistance of Copper Wire, 154.

Balmer Lines, The Broadening of the, of Hydrogen with Pressure, *E. O. Hulburt*, 112.

Barium Salts, The Relative Deposition of Radium and, as a Function of Temperature and Acidity, *W. B. Pietenpol*, 199.

Barnett, L. J. H., Improved Experiments on Magnetization by Rotation, 90.

Barnett, S. J., Improved Experiments on Magnetization by Rotation, 90.
  Note on the Cohn-Minkowski Formula for the Motion of Insulators in a Magnetic Field, 114.

Bateman, H., The Stress-Energy Tensor in Electromagnetic Theory and a New Law of Force, 243.

Becker, Joseph A., The Effect of a Magnetic Field on the Absorption of X-Rays, 115.
  The Effect of the Magnetic Field on the Absorption of X-Rays, 134.

Becknell, G. G., An Extension of the Principle of the Diffraction Evolute and Some of its Structural Detail, 594.
  An Extension of the Principle of the Diffraction Evolute, and Some of its Structural Detail, 201.
  Reciprocal Diffraction Relations be-

tween Circular and Elliptical Plates, 97.
Reciprocal Diffraction Relations between Circular and Elliptical Plates, 601.
Reciprocal Diffraction Relations between Circular and Elliptical Plates, 607.
Bismuth, Note on the Ratio of Mass to Weight for, and Aluminum, *H. A. Wilson*, 75.
Blackwood, Oswald, The Existence of High Mobility Ions, 499.
Boardman, Leland Jaynes, A Study of the Exciting Power for Fluorescence of the Different Parts of the Ultra-Violet Spectrum, 552.
Boner, C. P., Free Modes of Oscillation in Loop Aerials, 90.
Bow, The Action of the, in Stringed Instruments, *K. C. Kar*, 148.
Boynton, W. P., A Modification of Van der Waal's Equation, 46.
Breaking an Inductive Circuit, 199.
Brackett, F. S., Study of the Hydrogen Radiation in the Red and the Infrared, 111.
Bramley, Arthur, A Modification of Van der Waal's Equation, 46.
Brombacher, W. G., Detecting Efficiency of the Resistance-Capacity Coupled Amplifier to 6,000 Meters, 433.
Broxon, James W., Electrical Conduction Across Minute Air-Gaps, 476.
Brown, S. L., Free Modes of Oscillation in Loop Aerials, 90.
Burton, E. F., Test of Coagulative Power by Means of the Centrifuge, 197.

C.

Cadmium, The Hall-Ettingshausen, Nernst and Leduc Effects in, Nickel and Zinc, *A. E. Caswell*, 280.
Cady, W. G., Elastic Constants of Rods at High Frequencies, 98.
Calorimeter, A Flow, for Measuring the Heat Capacity of Gases, *H. F. Stimson, T. S. Sligh* and *N. S. Osborne*, 98.
Campbell, George A., Direct Capacity Measurement, 93.
Carbon Bisulphide, The Variation of the Index of Refraction of Water, Ethyl Alcohol, and, with the Temperature, *Elmer E. Hall* and *Arthur R. Payne*, 249.
Carman, A. P., A Second Undamped Wave Method of Determining Dielectric Constants, 715.
Caswell, A. E., The Hall-Ettingshausen, Nernst and Leduc Effects in Cadmium, Nickel and Zinc, 280.
Cathodoluminescence of Heated Alumina, *D. T. Wilber*, 101.
Centrifuge, Test of Coagulative Power by Means of the, *E. F. Burton* and *J. E. Currie*, 197.
Charges, The Ratio of the Two Elementary, *F. W. Loomis*, 15.
Clyde, Harry, The Capillary Potential Function and its Relation to Irrigation Practice, 196.
Coagulative Power, Test of, by Means of the Centrifuge, *E. F. Burton* and *J. E. Currie*, 197.
Coefficient in Solids, The Diffusion, and its Temperature Coefficient, *Saul Dushman* and *Irving Langmuir*, 113.
Cohn-Minkowski Formula, Note on the, for the Motion of Insulators in a Magnetic Field, *S. J. Barnett*, 114.
Collins, J. R., The Effect of Certain Dissolved Substances of the Infra-red Absorption of Water, 486.
Colloidal Particles, The Effect of Dissolved Substances on the Deposition of, from a Solution by Means of an Electric Current, *Richard D. Kleeman*, 272.
Compton, Karl T., Effect of the Initial Emission Velocities of Electrons on the Minimum Arcing Voltage in Gases, 105.
Theory of Ionization by Cumulative Action and the Low Voltage Arc, 283.
Concilio, A., Noises in Stressed Metals, 95.
Constants, The Optical, of Sodium-Potassium Alloys, *Raymond Morgan*, 204.
Contact Difference, Variation of, of Potential with Temperature in Potassium and Sodium, and the Accompanying Changes in Photoelectric Emission, *Herbert Ives*, 102.
Cooling, A Mathematical Study of Various Hypotheses on Rapid, *K. Heindlhofer*, 221.
Copper-Manganese Alloys, The Thermoelectromotive Force of, *Skezug Kimura* and *Zunehachi Isawa*, 441.
Copper Wire, A Study of the Effect of Adsorbed Gas on the High-Frequency Resistance of, *Austin Bailey*, 154.
Cork, J. M., A Characteristic X-Ray Absorption in the "L" Series for Elements N62 to N77, 81.
Coulson, John, An Extension of the Principle of the Diffraction Evolute and Some of its Structural Detail, 594.
An Extension of the Principle of the Diffraction Evolute, and Some of its Structural Detail, 201.
Reciprocal Diffraction Relations between Circular and Elliptical Plates, 601.
Reciprocal Diffraction Relations between Circular and Elliptical Plates, 97.
Reciprocal Diffraction Relations between Circular and Elliptical Plates, 607.
The Effect of Nascent Hydrogen on Hard Steel Magnets, 51.
Covariance, Maxwell's Law of Distribution of Velocities and the Principle of Projective, *I. Maizlish*, 39.

Critical Potentials, New Evidence Regarding the Interpretation of, in Hydrogen, *P. S. Olmstead*, 613.
Crystal Structure, The, of Silver-Palladium and Silver-Gold Alloys, *L. W. McKeehan*, 424.
Crystal Structure, The, of Strontium Selenide, *Mabel K. Slattery*, 84.
Clark, George L., A New Method of Using X-Rays in Crystal Analysis, 84.
Compton, Arthur P., Total Reflection of X-Rays from Glass and Silver, 84.
Crystals, The Scattering of X-Rays by, *G. E. M. Jauncey*, 405, 421.
Cumulative Action, Theory of Ionization by, and the Low Voltage Arc, *Karl T. Compton*, 283.
Currie, J. E., Test of Coagulative Power by Means of the Centrifuge, 197.
Cylinder, Heat Flow in a Finite, having Variable Surface Temperature, *George E. Thompson*, 601.

D.

Damon, Elizabeth E., Improvement in the Determination of the Radium Content of Low-Grade Radium-Barium Salts, 59.
Davey, Wheeler P., Precision Measurements of the Alkali Halides, 83.
Davisson, C., The Secondary Electron Emission from Nickel, 109.
The Thermionic Work Function of Tungsten, 300.
Dempster, A. J., Positive-Ray Analysis of Potassium, Calcium and Zinc, 631.
Diatomic Gases, Low Voltage Arcs in, *O. S. Duffendack*, 665.
Dielectric Constants, A Second Undamped Wave Method of Determining, *A. P. Carman* and *G. T. Lorance*, 715.
Diffraction Evolute, An Extension of the Principle of the, and Some of its Structural Detail, *G. G. Becknell* and *John Coulson*, 201.
Diffraction Evolute, An Extension of the Principle of the, and Some of its Structural Detail, *G. G. Becknell* and *John Coulson*, 594.
Diffraction Relations, Reciprocal, between Circular and Elliptical Plates, *John Coulson* and *G. G. Becknell*, 607.
Diffusion Coefficient, The, in Solids and its Temperature Coefficient, *Saul Dushman* and *Irving Langmuir*, 113.
Dimensional Invariants, Atomic Constants and, *A. C. Lunn*, 1.
Dispersion, An Experimental Investigation of the, of a Limited Wave Train, *Irvin H. Holt*, 513.
Distortion, Effect of the Current, by Long Lines on the Operating of Recording Relays, *Carl Kinsley*, 92.
Downey, K. Melvina, The Variation of the Residual Ionization in Air with Pressure, for a Range of 57 Atmospheres, 186.
Duane, A. R., The Scattering of X-Rays at Small Angles, 86.
Duane, William, A New Method of Using X-Rays in Crystal Analysis, 84.
A Study of Secondary Valence by Means of X-Rays, 85.
The Scattering of X-Rays at Small Angles, 86.
Duffendack, O. S., Excitation of the Spectra of Hydrogen and of Nitrogen in Low Voltage Arcs, 100.
Low Voltage Arcs in Diatomic Gases, 665.
Dushman, Saul, A General Relation for Electron Emission from Metals, 109.
The Diffusion Coefficient in Solids and its Temperature Coefficient, 113.

E.

Ear, The Relative Sensitivity of the, at Different Levels of Loudness, *Donald Mackenzie*, 331.
Edlefsen, N. E., The Capillary Potential Function and its Relation to Irrigation Practice, 196.
Efficiency, Detecting, of the Resistance-Capacity Coupled Amplifier to 6,000 Meters, *W. G. Brombacher*, 433.
Efflux of a Liquid, The Influence of the Surface Tension on the, in Jet-Form, *Julius Hartmann*, 99.
Elastic Constants of Rods at High Frequencies, *W. G. Cady*, 98.
Eldridge, John A., The Energy Losses Accompanying Ionization and Resonance in Mercury Vapor, 456.
Electrical Conduction Across Minute Air-Gaps, *James W. Broxon*, 476.
Electrical Conductivity, The, of Metallic Films when Exposed to Ultraviolet Light, *Orin Tugman*, 195.
Electric Charge, Oil-Drop Experiments as Proof of the Invariance of, *F. W. Loomis*, 111.
Electric Current. The Effect of Dissolved Substances on the Deposition of Colloidal Particles from a Solution by Means of an, *Richard D. Kleeman*, 272.
Electric Waves, Short, *E. F.* , 88.
Electric Waves, The Optical Constants of Certain Liquids for Short, *J. D. Tear*, 88.
Electron Emission, The, from Thoriated Tungsten Filaments, *Irving Langmuir*, 106.
Electrons, Bombardment of Metal Surfaces by Slow-Moving, *H. E. Farnsworth*, 358.
Electrons, Effect of the Initial Emission Velocities of, on the Minimum Arcing Voltage in Gases, *K. T. Compton* and *Y. T. Yao*, 105.
Electrons, Mobilities of, in Hydrogen, *Leonard B. Loeb*, 106.
Electrons, On the Effect of Short Electromagnetic Waves on a Beam of, *C. J. Lapp*, 104.

Electrons, Radiation from a Group of, *Leigh Page*, 18.
Electrons, The Mobilities of, in Hydrogen, *Leonard B. Loeb*, 397.
Electrostatic Charge. The Variation of Metallic Conductivity with, *F. Wenner*, *Nyna L. Forman* and *A. R. Lindberg*, 589.
Energy Distribution in Continuous X-Ray Spectra, *Paul Kirkpatrick*, 197.
Energy Losses, The, Accompanying Ionization and Resonance in Mercury Vapor, *John A. Eldridge*, 456.
Erikson, Henry A., On the Nature of the Negative and Positive Ions in Air, Oxygen and Nitrogen, 117.
Erratum, 745.
Ether-Drift Experiment, Another, *Roy J. Kennedy*, 26.
Ethyl Alcohol, The Variation of the Index of Refraction of Water, and Carbon Bisulphide, with the Temperature, *Elmer E. Hall* and *Arthur R. Payne*, 249.
Electromagnetic Theory, The Stress-Energy Tensor in, and a New Law of Force, *H. Bateman*, 243.
Electromagnetic Waves in Absorbing Media, *Leigh Page*, 166.
Electromagnetic Waves, On the Effect of Short, on a Beam of Electrons, *C. J. Lapp*, 104.
Electromotive Force, A Transition of Adsorption-Layer Theory of the, of the Voltaic Cell, *R. D. Kleeman*, 174.
Electron, An Experimental Method of Testing the Expressions for Longitudinal and Transverse Masses of the, *L. T. Jones* and *W. C. Pomeroy*, 110.
Electron Emission, A General Relation for, from Metals, *Saul Dushman*, 109.
Electron Emission, The Secondary, from Nickel, *C. Davisson* and *C. H. Kunsman*, 109.
Electron, Note on the Lorentzian, *I. Maislish*, 34.
Electron, Note on the Size of the, as Determined by the Absorption and Scattering of X-Rays, *F. K. Richtmyer*, 87.
Electron Tubes, The Measurement of Magnetic Field Strength by Means of, *Albert W. Hull*, 108.

F.

Farnsworth, H. E., Bombardment of Metal Surfaces by Slow-Moving Electrons, 358.
Fluorescence, A Study of the Exciting Power for, of the Different Parts of the Ultraviolet Spectrum, *Leland Jaynes Boardman*, 552.
Foley, Arthur L., A Photographic Study of Sound Pulses between Curved Walls and Sound Amplification by Horns, 505.
Force, The Stress-Energy Tensor in Electromagnetic Theory and a New Law of, *H. Bateman*, 243.
Forman, Nyna L., The Variation of Metallic Conductivity with Electrostatic Charge, 589.
Foote, Paul D., X-Ray Limits beyond the Range of Spectroscopic Measurements, 82.
Forsythe, W. E., Radiation from Oxides. I. Emissive Power of Zirconium Oxide, 101.
Foster, John Stuart, The Relative Intensities of Stark Effect Components in the Helium Spectrum, 100.
  Relative Intensities of Stark Effect Components in the Helium Spectrum, 214.
Frayne, John G., The Reversible Inductivity of Rochelle Salt under High Frequency Fields, 97.
Fry, Thornton C., The Voltage-current Relation in Central Anode Photo-electric Cells, 112.

G.

Gaehr, Paul F., Note on the Specific Heat of Tungsten, 375.
Gardner, Willard, A New Method of Mechanical Analysis of Soils, 196.
  The Capillary Potential Function and its Relation to Irrigation Practice, 196.
Gases, Phenomena in, Excited by Radio-Frequency Currents, *E. O. Hulburt*, 127.
Germanium, Crystal Structures of Vanadium, and Graphite, *Albert W. Hull*, 113.
Germer, L. H., The Thermionic Work Function of Tungsten, 300.
Ghosh, R. N., Note on Musical Drums, 526.
  Note on Overblown Pipes, 452.
Gibson, George E., A Study of the Luminous Discharge in Hydrogen and in Mercury and a New Method of Measuring Ionization Potentials, 99.
Glass, Total Reflection of X-Rays from, and Silver, *Arthur P. Compton*, 84.
Graphite, Crystal Structures of Vanadium, Germanium and, *Albert W. Hull*, 113.
Grover, Frederick W., The Calculation of the Capacity of Antennas, 92.

H.

Halides, Precision Measurements of the Alkali, *Wheeler P. Davey*, 83.
Hall, Elmer E., The Variation of the Index of Refraction of Water, Ethyl Alcohol, and Carbon Bisulphide, with the Temperature, 243.
Hall-Ettingshausen, The, Nernst and Leduc Effects in Cadmium, Nickel and Zinc, *A. E. Caswell*, 280.
Hamer, Richard, The Limiting Frequency of the Photo-electric Effect, 198.
Harrison, George R., The Absorption of Light by Sodium Vapor, 198.

Hartmann, Julius, The Influence of the Surface Tension of the Efflux of a Liquid in Jet-Form, 99.
  A New Method for the Generation of Sound Waves, 114.
  On a New Method for the Generation of Sound Waves, 719.
  On the Influence of the Surface-Tension on the Efflux of a Liquid in Jet-Form, 728.
Heat Capacity, A Flow Calorimeter for Measuring the, of Gases, *H. F. Stimson*, *T. S. Sligh* and *N. S. Osborne*, 98.
Heat Flow in a Finite Cylinder having Variable Surface Temperature, *George E. Thompson*, 601.
Heindlhofer, K., Quenching: A Mathematical Study of Various Hypotheses on Rapid Cooling, 221.
Helium, Formation and Life of Metastable, *Fabian M. Kannenstine*, 115.
Helium Spectrum, Relative Intensities of Stark Effect Components in the, *John Stuart Foster*, 214.
Hess, Victor F., Improvement in the Determination of the Radium Content of Low-Grade Radium-Barium Salts, 59.
Hewlett, C. W., An Experimental Study of the Scattering of Approximately Homogeneous X-Rays by Powdered Crystalline Carbon, Metallic Lithium, and Liquid Benzene, Mesitylene and Octave, 688.
High Frequencies, Elastic Constants of Rods at, *W. G. Cady*, 98.
High-Frequency Fields, The Reversible Inductivity of Rochelle Salt under, *John G. Frayne*, 97.
Hill, Charles F., Measurement of Mercury-Vapor Pressure by Means of the Knudsen Pressure Gauge, 259.
Holt, Irvin H., An Experimental Investigation of the Dispersion of a Limited Wave Train, 513.
Hopfield, J. J., Spectra of Hydrogen, Nitrogen and Oxygen in the Extreme Ultraviolet, 573.
Hulburt, E. O., The Broadening of the Balmer Lines of Hydrogen with Pressure, 112.
  Phenomena in Gases Excited by Radio-Frequency Currents, 104.
  Phenomena in Gases Excited by Radio-Frequency Currents, 127.
Hull, Albert W., Crystal Structures of Vanadium, Germanium and Graphite, 113.
  The Measurement of Magnetic Field Strength by Means of Electron Tubes, 108.
Hydrogen, A Study of the Luminous Discharge in, and in Mercury and a New Method of Measuring Ionization Potentials, *George E. Gibson* and *W. Albert Noyes, Jr.*, 99.
Hydrogen, Excitation of the Spectra of, and of Nitrogen in Low-Voltage Arcs, *O. S. Duffendack*, 100.
Hydrogen, Mobilities of Electrons in, *Leonard B. Loeb*, 106.
Hydrogen, The Effect of Occluded, upon the Crystalline Space-Lattice of Palladium, *L. W. McKeehan*, 82.
Hydrogen, The Broadening of the Balmer Lines of, with Pressure, *E. O. Hulburt*, 112.
Hydrogen, New Evidence Regarding the Interpretation of Critical Potentials in, *P. S. Olmstead*, 613.
Hydrogen, The Mobilities of Electrons in, *Leonard B. Loeb*, 397.
Hydrogen, New Evidence Regarding the Interpretation of Critical Potentials in, *P. S. Olmstead*, 613.
Hydrogen Radiation, Study of the, in the Red and the Infra-Red, *F. S. Brackett*, 111.
Hygroscopicity, The, of Soil, *M. D. Thomas*, 201.
Hypotheses, A Mathematical Study of Various, on Rapid Cooling, *K. Heindlhofer*, 221.
Hysteresis, A Mechanical Model for, *A. Press*, 89.

I.

Illuminants, The Complete Scale of Color Temperature and its Application to the Color Grading of Daylight and Artificial, *Irwin G. Priest*, 93.
Incandescent Temperatures, The Simple Rigidity of a Drawn Tungsten Wire at, *William Schriever*, 96.
Index, 747.
Inductive Circuit, Breaking an, *W. P. Boynton*, 199.
Insulators, Note on the Cohn-Minkowski Formula for the Motion of, in a Magnetic Field, *S. J. Barnett*, 114.
Intensities, Relative, of Stark Effect Components in the Helium Spectrum, *John Stuart Foster*, 214.
Intensity of Radiation, Specific, in an Absorbing Medium, *Leigh Page*, 103.
Invariants, Atomic Constants and Dimensional, *A. C. Lunn*, 1.
Ions, On the Nature of the Negative and Positive, in Air, Oxygen and Nitrogen, 117.
Ions, The Existence of High Mobility, *Oswald Blackwood*, 499.
Ionization in Air, The Variation of the Residual, with Pressure, for a Range of 57 Atmospheres, *K. Melvina Downey*, 186.
Ionization, Theory of, by Cumulative Action and the Low-Voltage Arc, *Karl T. Compton*, 283.
Ionization, The Energy Losses Accompanying, and Resonance in Mercury Vapor, *John A. Eldridge*, 456.
Irrigation Practice, The Capillary Potential Function and its Relation to, *Willard Gardner*, *O. W. Israelsen*, *N. E. Edlefsen* and *Harry Clyde*, 196.

Isawa, Zunehachi, The Thermoelectromotive Force of Copper-Manganese Alloys, 441.
Israelsen, O. W., The Capillary Potential Function and its Relation to Irrigation Practice, 196.
Ives, Herbert, Variation of Contact Difference of Potential with Temperature in Potassium and Sodium, and the Accompanying Changes in Photo-electric Emission, 102.
Ives, Herbert E., The Voltage-current Relation in Central Anode Photo-electric Cells, 112.

J.

Jauncey, G. E. M., Effect of Temperature on the X-Rays Scattered by Crystals, 82.
 The Scattering of X-Rays by Crystals, 405.
 The Effect of Temperature on the Scattering of X-Rays by Crystals, 421.
Jennings, D. S., A New Method of Mechanical Analysis of Soils, 196.
Jones, L. T., An Experimental Method of Testing the Expressions for Longitudinal and Transverse Masses of the Electron, 110.

K.

Kannenstine, Fabian M., Formation and Life of Metastable Helium, 115.
Kar, K. C., The Action of the Bow in Stringed Instruments, 148.
Kennedy, Roy J., Another Ether-Drift Experiment, 26.
Kent, C. V., The Effect of a Longitudinal Magnetic Field on the Mechanical Properties of a Vibrating Nickel Wire, 91.
Kimura, Skezug, The Thermoelectromotive Force of Copper-Manganese Alloys, 441.
Kingdon, K. H., The Removal of Thorium from the Surface of a Thoriated Tungsten Filament by Bombardment with Positive Ions, 108.
Kinsley, Carl, Effect of the Current Distortion by Long Lines on the Operating of Recording Relays, 92.
Kirkpatrick, Paul, Energy Distribution in Continuous X-Ray Spectra, 197.
Kleeman, Richard D., A Transition of Adsorption-Layer Theory of the E.M.F. of the Voltaic Cell, 174.
 The Effect of Dissolved Substances on the Deposition of Colloidal Particles from a Solution by Means of an Electric Current, 272.
Knudsen Pressure Gauge, Measurement of Mercury-Vapor Pressure by Means of the, *Charles F. Hill*, 259.
Kunsman, C. H., The Secondary Electron Emission from Nickel, 109.

L.

Langmuir, Irving, The Electron Emission from Thoriated Tungsten Filaments, 106.
 Radial Flow in Rotating Liquids, 95.
 The Removal of Thorium from the Surface of a Thoriated Tungsten Filament by Bombardment with Positive Ions, 108.
 The Diffusion Coefficient in Solids and its Temperature Coefficient, 113.
Lapp, C. J., On the Effect of Short Electromagnetic Waves on a Beam of Electrons, 104.
Leduc Effects, The Hall-Ettingshausen, Nernst and, in Cadmium, Nickel and Zinc, *A. E. Caswell*, 280.
Lenzen, V. F., A General Method of Determining the Adiabatic Invariants of Mechanical Systems, 201.
Light, The Absorption of, by Sodium Vapor, *George R. Harrison*, 198.
Lindberg, A. R., The Variation of Metallic Conductivity with Electrostatic Charge, 589.
Liquid Benzene Mesitylene, An Experimental Study of the Scattering of Approximately Homogeneous X-Rays by Powdered Crystalline Carbon, and Octave, *C. W. Hewlett*, 688.
Liquid Surface, The Effect of, upon the Arcing Voltage in Mercury Vapor, *Y. T. Yao*, 105.
Loeb, Leonard B., Mobilities of Electrons in Hydrogen, 106.
 The Mobilities of Electrons in Hydrogen, 397.
Loomis, F. W., The Ratio of the Two Elementary Charges, 15.
 Oil-Drop Experiments as Proof of the Invariance of Electric Charge, 111.
Lorance, G. T., A Second Undamped Wave Method of Determining Dielectric Constants, 715.
Lorentzian Electron, Note on the, *I. Maizlish*, 34.
Low Voltage Arcs, Excitation of the Spectra of Hydrogen and of Nitrogen in, *O. S. Duffendack*, 100.
Low Voltage Arcs in Diatomic Gases, *O. S. Duffendack*, 665.
Luminous Discharge, A Study of the, in Hydrogen and in Mercury and a New Method of Measuring Ionization Potentials, *George E. Gibson* and *W. Albert Noyes, Jr.*, 99.
Lunn, A. C., Atomic Constants and Dimensional Invariants, 1.

M.

McKeehan, L. W., The Effect of Occluded Hydrogen upon the Crystalline Space-Lattice of Palladium, 82.
 The Crystal Structure of Silver-Palladium and Silver-Gold Alloys, 424.

MacNutt, Barry, Noises in Stressed Metals, 95.
Mackenzie, Donald, The Relative Sensitivity of the Ear at Different Levels of Loudness, 331.
Magnetic Field Strength, The Measurement of, by Means of Electron Tubes, *Albert W. Hull*, 108.
Magnetic Field, The Effect of a Longitudinal, on the Mechanical Properties of a Vibrating Nickel Wire, *C. V. Kent* and *B. J. Babbitt*, 91.
Magnetic Field, The Effect of the, on the Absorption of X-Rays, *Joseph A. Becker*, 134.
Magnetization, Improved Experiments on, by Rotation, *S. J. Barnett* and *L. J. H. Barnett*, 90.
Magnets, The Effect of Nascent Hydrogen on Hard Steel, *John Coulson*, 51.
Maizlish, I., Note on the Lorentzian Electron, 34.
Maxwell's Law of Distribution of Velocities and the Principle of Projective Covariance, 39.
Maxwell's Law of Distribution of Velocities and the Principle of Projective Covariance, *I. Maizlish*, 39.
Measurement, Direct Capacity, *George A. Campbell*, 93.
Mercury, A Study of the Luminous Discharge in Hydrogen and in, and a New Method of Measuring Ionization Potentials, *George E. Gibson* and *W. Albert Noyes, Jr.*, 99.
Mercury Vapor, The Effect of Liquid Surface upon the Arcing Voltage in, *Y. T. Yao*, 105.
Mercury-Vapor Pressure, Measurement of, by Means of the Knudsen Pressure Gauge, *Charles F. Hill*, 259.
Mercury Vapor, The Energy Losses Accompanying Ionization and Resonance in, *John A. Eldridge*, 456.
Metal, The Variation of the Photoelectric Current with Thickness of, *Otto Stuhlman, Jr.*, 65.
Metallic Conductivity, The Variation of, with Electrostatic Charge, *F. Wenner, Nyna L. Forman* and *A. R. Lindberg*, 589.
Metallic Films, The Electrical Conductivity of, when Exposed to Ultraviolet Light, *Orin Tugman*, 195.
Metallic Lithium, An Experimental Study of the Scattering of Approximately Homogeneous X-Rays by Powdered Crystalline Carbon, and Liquid Benzene Mesitylene and Octave, *C. W. Hewlett*, 688.
Metals, Noises in Stressed, *Barry MacNutt* and *A. Concilio*, 95.
Metal Surfaces, Bombardment of, by Slow-Moving Electrons, *H. E. Farnsworth*, 358.
Millikan, R. A., New Proof of the Specular Reflection of Molecules, 95.
Mobility, On the Ageing Effect in the, of Positive Gas Ions, *H. B. Wahlin*, 267.
Molecules, New Proof of the Specular Reflection of, *R. A. Millikan* and *Karl S. Van Dyke*, 95.
Molten Glass, A Simple and Accurate Method for Determining Surface Tension and Density of, *Edward W. Washburn*, 94.
Molten Metals, The Optical Properties of, *A. K. Aster*, 349.
Mohler, F. L., X-Ray Limits beyond the Range of Spectroscopic Measurements, 82.
Morgan, Raymond, The Optical Constants of Sodium-Potassium Alloys, 204.
Mottsmith, Harold, Radial Flow in Rotating Liquids, 95.
Musical Drums, Note on, *R. N. Ghosh*, 526.

N.

Nascent Hydrogen, The Effect of, on Hard Steel Magnets, *John Coulson*, 51.
Nernst, The Hall-Ettingshausen, and Leduc Effects in Cadmium, Nickel and Zinc, *A. E. Caswell*, 280.
Nichols, E. F., Short Electric Waves, 88.
Nickel, The Secondary Electron Emission from, *C. Davisson* and *C. H. Kunsman*, 109.
Nickel, The Hall-Ettingshausen, Nernst and Leduc Effects in Cadmium, and Zinc, *A. E. Caswell*, 280.
Nitrogen, Excitation of the Spectra of Hydrogen and of, in Low Voltage Arcs, *O. S. Duffendack*, 100.
Nitrogen, On the Nature of the Negative and Positive Ions in Air, Oxygen and, *Henry A. Erikson*, 117.
Nitrogen, Spectra of Hydrogen, and Oxygen in the Extreme Ultraviolet, *J. J. Hopfield*, 573.
Noyes, W. Albert, Jr., A Study of the Luminous Discharge in Hydrogen and in Mercury and a New Method of Measuring Ionization Potentials, 99.

O.

Octave, An Experimental Study of the Scattering of Approximately Homogeneous X-Rays by Powdered Crystalline Carbon, Metallic Lithium, and Liquid Benzene Mesitylene and, *C. W. Hewlett*, 688.
Oil-Drop Experiments as Proof of the Invariance of Electric Charge, *F. W. Loomis*, 111.
Olmstead, P. S., New Evidence Regarding the Interpretation of Critical Potentials in Hydrogen, 613.
Optical Constants, The, of Certain Liquids for Short Electric Waves, *J. D. Tear*, 88.
Osborne, N. S., A Flow Calorimeter for Measuring the Heat Capacity of Gases, 98.

Oscillation, Free Modes of, in Loop Aerials, *S. L. Brown*, 90.

Overblown Pipes, Notes on, *S. Shargava* and *R. N. Ghosh*, 452.

Oxygen, On the Nature of the Negative and Positive Ions in Air, and Nitrogen, *Henry A. Erikson*, 117.

Oxygen, Spectra of Hydrogen, Nitrogen and, in the Extreme Ultraviolet, *J. J. Hopfield*, 573.

P.

Page, Leigh, Radiation from a Group of Electrons, 18.
  Specific Intensity of Radiation in an Absorbing Medium, 103.
  Electromagnetic Waves in Absorbing Media, 166.

Palladium, The Effect of Occluded Hydrogen upon the Crystalline Space-Lattice of, *L. W. McKeehan*, 82.

Payne, Arthur R., The Variation of the Index of Refraction of Water, Ethyl Alcohol, and Carbon Bisulphide, with the Temperature, 243.

Pfund, A. H., A Precision Rotating Sector: Aperture Variable and Measurable while in Motion, 103.

Photo-electric Cells, The Voltage-current Relation in Central Anode, *Herbert E. Ives* and *Thornton C. Fry*, 112.

Photoelectric Current, The Variation of the, with Thickness of Metal, *Otto Stuhlman, Jr.*, 65.

Photo-electric Effect, The Limiting Frequency of the, *Richard Hamer*, 198.

Photo-electric Emission, Variation of Contact Difference of Potential with Temperatures in Potassium and Sodium, and the Accompanying Changes in, *Herbert Ives*, 102.

Photoelectronic Velocities, Symmetry of Emergent and Incident, *Robert James Piersol*, 195.

Piersol, Robert James, Symmetry of Emergent and Incident Photoelectronic Velocities, 195.

Pietenpol, W. B., The Relative Deposition of Radium and Barium Salts as a Function of Temperature and Acidity, 199.

Piezo-electric Effect, Properties of Rochelle Salt related to the, *Joseph Valasek*, 639.

Pipes, Note on Overblown, *S. Shargava* and *R. N. Ghosh*, 452.

Plates, Reciprocal Diffraction Relations between Circular and Elliptical, *John Coulson* and *G. G. Becknell*, 97.

Pomeroy, W. C., An Experimental Method of Testing the Expressions for Longitudinal and Transverse Masses of the Electron, 110.

Positive Ions, The Removal of Thorium from the Surface of a Thoriated Tungsten Filament by Bombardment with, *K. H. Kingdon* and *Irving Langmuir*, 108.

Positive Gas Ions, On the Ageing Effect in the Mobility of, *H. B. Wahlin*, 267.

Positive-Ray Analysis of Potassium Calcium and Zinc, *A. J. Dempster*, 631.

Potassium Calcium, Positive-Ray Analysis of, and Zinc, *A. J. Dempster*, 631.

Potential Function, The Capillary, and its Relation to Irrigation Practice, *Willard Gardner*, *O. W. Israelsen*, *N. E. Edlefsen* and *Harry Clyde*, 196.

Powdered Crystalline Carbon, An Experimental Study of the Scattering of Approximately Homogeneous X-Rays by Metallic Lithium, and Liquid Benzene Mesitylene and Octave, *C. W. Hewlett*, 688.

Precision Measurements of the Alkali Halides, *Wheeler P. Davey*, 83.

Precision Rotating Sector, A: Aperture Variable and Measurable while in Motion, *A. H. Pfund*, 103.

Press, A., A Mechanical Model for Hysteresis, 89.

Priest, Irwin G., The Complete Scale of Color Temperature and its Application to the Color Grading of Daylight and Artificial Illuminants, 93.

Projective Covariance, Maxwell's Law of Distribution of Velocities and the Principle of, *I. Maizlish*, 39.

Q.

Quenching: A Mathematical Study of Various Hypotheses on Rapid Cooling, 221.

R.

Radial Flow in Rotating Liquids, *Harold Mottsmith* and *Irving Langmuir*, 95.

Radiation, Specific Intensity of, in an Absorbing Medium, *Leigh Page*, 103.

Radiation from a Group of Electrons, *Leigh Page*, 18.

Radiation from Oxides. I. Emissive Power of Zirconium Oxide, *W. E. Forsythe*, 101.

Radii of the Atoms of the Alkali Metal Vapors, *S. H. Anderson*, 200.

Radio-Frequency Currents, Phenomena in Gases Excited by, *E. O. Hulburt*, 104.

Radio-Frequency Currents, Phenomena in Gases Excited by, *E. O. Hulburt*, 127.

Radium, The Relative Deposition of, and Barium Salts as a Function of Temperature and Acidity, *W. B. Pietenpol*, 199.

Radium Content, Improvement in the Determination of the, of Low-Grade Radium Barium Salts, *Victor F. Hess* and *Elizabeth E. Damon*, 59.

Reciprocal Diffraction Relations between Circular and Elliptical Plates, *John Coulson* and *G. G. Becknell*, 97.

Refraction of Water, The Variation of the Index of, Ethyl Alcohol, and Carbon

Bisulphide, with the Temperature, *Elmer E. Hall* and *Arthur R. Payne*, 249.
Residual Ionization, The Variation of the, in Air with Pressure, for a Range of 57 Atmospheres, *K. Melvina Downey*, 186.
Resistance, A Study of the Effect of Adsorbed Gas on the High-Frequency, of Copper Wire, *Austin Bailey*, 154.
Resistance-Capacity, Detecting Efficiency of the, Coupled Amplifier to 6,000 Meters, *W. G. Brombacher*, 433.
Resonance, The Energy Losses Accompanying Ionization and, in Mercury Vapor, *John A. Eldridge*, 456.
Richtmyer, F. K., Note on the Size of the Electron as Determined by the Absorption and Scattering of X-Rays, 87.
Rochelle Salt, The Reversible Inductivity of, under High-Frequency Fields, *John G. Frayne*, 97.
Rochelle Salt, Properties of, related to the Piezo-electric Effect, *Joseph Valasek*, 639.
Rotating Liquids, Radial Flow in, *Harold Mottsmith* and *Irving Langmuir*, 95.

S.

Schriever, William, The Simple Rigidity of a Drawn Tungsten Wire at Incandescent Temperatures, 96.
Sensitivity, The Relative, of the Ear at Different Levels of Loudness, *Donald Mackenzie*, 331.
Shargava, S., Note on Overblown Pipes, 452.
Silver, Total Reflection of X-Rays from Glass and, *Arthur P. Compton*, 84.
Silver-Gold Alloys, The Crystal Structure of Silver-Palladium and, *L. W. McKeehan*, 424.
Silver-Palladium, The Crystal Structure of, and Silver-Gold Alloys, *L. W. McKeehan*, 424.
Slattery, Mabel K., The Crystal Structure of Strontium Selenide, 84.
Sligh, T. S., A Flow Calorimeter for Measuring the Heat Capacity of Gases, 98.
Sodium Vapor, The Absorption of Light by, *George R. Harrison*, 198.
Sound Amplification, A Photographic Study of Sound Pulses between Curved Walls and, by Horns, *Arthur L. Foley*, 505.
Sound Pulses, A Photographic Study of, between Curved Walls and Sound Amplification by Horns, *Arthur L. Foley*, 505.
Sound Waves, On a New Method for the Generation of, *Julius Hartmann*, 719.
Sound Waves, A New Method for the Generation of, *Julius Hartmann*, 114.
Specific Heat, Note on the, of Tungsten, *Paul F. Gaehr*, 375.
Specific Intensity of Radiation in an Absorbing Medium, *Leigh Page*, 103.
Spectroscopic Measurements, X-Ray Limits beyond the Range of, *F. L. Mohler* and *Paul D. Foote*, 82.
Specular Reflection, New Proof of the, of Molecules, *R. A. Millikan* and *Karl S. Van Dyke*, 95.
Stark Effect Components, The Relative Intensities of, in the Helium Spectrum, *John Stuart Foster*, 100.
Stark Effect Components, Relative Intensities of, in the Helium Spectrum, *John Stuart Foster*, 214.
Stewart, G. W., Acoustic Wave Filters, 528.
Stimson, H. F., A Flow Calorimeter for Measuring the Heat Capacity of Gases, 98.
Stress-Energy Tensor, The, in Electromagnetic Theory and a New Law of Force, *H. Bateman*, 243.
Strontium Selenide, The Crystal Structure of, *Mabel K. Slattery*, 84.
Stuhlman, Jr., Otto, The Variation of the Photoelectric Current with Thickness of Metal, 65.
  The Variation of the Photoelectric Current with Thickness of Metal, 89.
Surface Temperature, Heat Flow in a Finite Cylinder having Variable, *George E. Thompson*, 601.
Surface Tension, A Simple and Accurate Method for Determining, and Density of Molten Glass, *Edward W. Washburn*, 94.
Surface Tension, The Influence of the, on the Efflux of a Liquid in Jet-Form, *Julius Hartmann*, 99.
Surface-Tension, On the Influence of the, on the Efflux of a Liquid in Jet-Form, *Julius Hartmann*, 728.

T.

Taylor, E. G., Absorption Coefficients for Homogeneous X-Rays, 709.
Tear, J. D., The Optical Constants of Certain Liquids for Short Electric Waves, 88.
  Short Electric Waves, 88.
Temperature, The Relative Deposition of Radium and Barium Salts as a Function of, and Acidity, *W. B. Pietenpol*, 199.
Temperature, The Effect of, on the Scattering of X-Rays by Crystals, *G. E. M. Jauncey*, 421.
Temperature Coefficient, The Diffusion Coefficient in Solids and its, *Saul Dushman* and *Irving Langmuir*, 113.
Thermoelectromotive Force, The, of Copper-Manganese Alloys, *Skesug Kimura* and *Zunehachi Isawa*, 441.
Thermionic Work Function, The, of Tungsten, *C. Davisson* and *L. H. Germer*, 300.
Thomas, M. D., A New Method of Mechanical Analysis of Soils, 196.
  The Hygroscopicity of Soil, 201,

Thompson, George E., Heat Flow in a Finite Cylinder having Variable Surface Temperature, 601.

Thorium, The Removal of, from the Surface of a Thoriated Tungsten Filament by Bombardment with Positive Ions, *K. H. Kingdon* and *Irving Langmuir*, 108.

Tugman, Orin, The Electrical Conductivity of Metallic Films when Exposed to Ultraviolet Light, 195.

Tungsten, The Thermionic Work Function of, *C. Davisson* and *L. H. Germer*, 300.

Tungsten, Note on the Specific Heat of, *Paul F. Gaehr*, 375.

Tungsten Filament, The Removal of Thorium from the Surface of a Thoriated, by Bombardment with Positive Ions, *K. H. Kingdon* and *Irving Langmuir*, 108.

Tungsten Filaments, The Electron Emission from Thoriated, *Irving Langmuir*, 106.

Tungsten Filaments, Theory of End-Loss Corrections and their Application to, in Vacuo, *A. G. Worthing*, 91.

Tungsten Wire, The Simple Rigidity of a Drawn, at Incandescent Temperatures, *William Schriever*, 96.

U.

Ultraviolet Light, The Electrical Conductivity of Metallic Films when Exposed to, *Orin Tugman*, 195.

Ultraviolet Spectrum, A Study of the Exciting Power for Fluorescence of the Different Parts of the, *Leland Jaynes Boardman*, 552.

V.

Valasek, Joseph, Properties of Rochelle Salt related to the Piezo-electric Effect, 639.

Vanadium, Crystal Structures of, Germanium and Graphite, *Albert W. Hull*, 113.

Van der Waal's Equation, A Modification of, *W. P. Boynton* and *Arthur Bramley*, 46.

Van Dyke, Karl S., New Proof of the Specular Reflection of Molecules, 95.

Velocities, Maxwell's Law of Distribution of, and the Principle of Projective Covariance, *I. Maizlish*, 39.

Velocities of Electrons, Effect of the Initial Emission, on the Minimum Arcing Voltage in Gases, *K. T. Compton* and *Y. T. Yao*, 105.

Voltaic Cell, A Transition of Adsorption-Layer Theory of the E.M.F. of the, *R. D. Kleeman*, 174.

W.

Wahlin, H. B., On the Ageing Effect in the Mobility of Positive Gas Ions, 267.

Washburn, Edward W., A Simple and Accurate Method for Determining Surface Tension and Density of Molten Glass, 94.

Wave Filters, Acoustic, *G. W. Stewart*, 528.

Wave Method, A Second Undamped, of Determining Dielectric Constants, *A. P. Carman* and *G. T. Lorance*, 715.

Wave Train, An Experimental Investigation of the Dispersion of a Limited, *Irvin H. Holt*, 513.

Wenner, F., The Variation of Metallic Conductivity with Electrostatic Charge, 589.

Wilber, D. T., Cathodoluminescence of Heated Alumina, 101.

Wilson, H. A., Note on the Ratio of Mass to Weight for Bismuth and Aluminum, 75.

Worthing, A. G., Theory of End-Loss Corrections and their Application to Tungsten Filaments in Vacuo, 91.

X.

X-Ray Absorption, Characteristic, in the "L" Series for Elements N62 to N77, *J. M. Cork*, 81.

X-Ray Limits beyond the Range of Spectroscopic Measurements, *F. L. Mohler* and *Paul D. Foote*, 82.

X-Rays, Absorption Coefficients for Homogeneous, *E. G. Taylor*, 709.

X-Ray Spectra, Energy Distribution in Continuous, *Paul Kirkpatrick*, 197.

X-Rays, A New Method of Using, in Crystal Analysis, *George L. Clark*, 85.

X-Rays, An Experimental Study of the Scattering of Approximately Homogeneous, by Powdered Crystalline Carbon, Metallic Lithium, and Liquid Benzene Mesitylene and Octave, *C. W. Hewlett*, 688.

X-Rays, A Study of Secondary Valence by Means of X-Rays, *William Duane*, 85.

X-Rays, Effect of Temperature on the, Scattered by Crystals, *G. E. M. Jauncey*, 82.

X-Rays, Note on the Size of the Electron as Determined by the Absorption and Scattering of, *F. K. Richtmyer*, 87.

X-Rays, The Effect of a Magnetic Field on the Absorption of, *Joseph A. Becker*, 115.

X-Rays, The Effect of the Magnetic Field on the Absorption of, *Joseph A. Becker*, 134.

X-Rays, The Scattering of, by Crystals, *G. E. M. Jauncey*, 405, 421.

X-Rays, Total Reflection of, from Glass and Silver, *Arthur P. Compton*, 84.

Y.

Yao, Y. T., Effect of the Initial Emission Velocities of Electrons on the Minimum Arcing Voltage in Gases, 105.
The Effect of Liquid Surface upon the

22

Arcing Voltage in Mercury Vapor, 105.

Z.

Zinc, Positive-Ray Analysis of Potassium Calcium and, *A. J. Dempster*, 631.

Zinc, The Hall-Ettingshausen, Nernst and Leduc Effects in Cadmium, Nickel and, *A. E. Caswell*, 280.

Zirconium Oxide. Radiation from Oxides. I. Emissive Power of, *W. E. Forsythe*, 101.

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